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Report RMD 5043-64-F

Contract No. NOnr 4364(00)

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ADVANCED OXIDIZER RESEARCH

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Report Period: 1 January 1964 to 31 December 1964

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ADVANCED OXIDIZER RESEARCH

Report RMD 5043-64-F

Report Period: 1 January 1964 to 31 December 1964

Contract No. NOnr 4364(00), ARPA Order No. 417

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GENERAL FOREWORD

This final report was prepared by Thiokol Chemical Corporation, Reaction Motors Division, Denville, New Jersey, and summarizes work in the area of advanced oxidizer chemistry conducted at this Division under the sponsorship of the Advanced Research Projects Agency from 1 January 1964 through 31 December 1964. The work was administered by the Department of the Navy, Office of Naval Research, with Mr. R. L. Hanson serving as Scientific Officer, and includes the following tasks:

Section	Task No.	Title
I	51	Difluoramine Chemistry
II	52	Synthesis of Compounds for Structure-Sensitivity Study
III	53	Chemistry of the Oxygen Subfluorides
IV	54	Stabilization of Nitronium Perchlorate
V	55	Thermal Stability of Advanced Solid Oxidizers
VI	56	Chemistry of Difluorodiazine and Nitrosyl Perchlorate

ABSTRACT

This report describes research conducted at Thiokol Chemical Corporation, Reaction Motors Division, directed toward the development of advanced solid oxidizers. The six major tasks on which work has been performed are listed below, together with an abstract of each task, and are included as six separate sections of this report.

SECTION I - DIFLUORAMINE CHEMISTRY

A mixture of 1, 2-bis(difluoramino)cyclohexene-3 and 1, 4-bis(difluoramino)-cyclohexene-2 was obtained by the addition of tetrafluorohydrazine to 1,3-cyclohexadiene. The mixture decolorized bromine solution and reacted with permanganate to yield carboxyl derivatives. Dehydrofluorination with an anionic exchange resin produced a conjugated difluorimine having interesting photochemical properties.

1,2-Difluoriminocyclohexane was prepared by the reaction of tetrafluorohydrazine with cyclohexene, followed by dehydrofluorination of the resulting bis(difluoramine). The difluorimine was decomposed by aqueous sodium hydroxide but remained unreactive toward concentrated sulfuric acid. Efforts to bring about addition reactions with tetrafluorohydrazine and isocyanic acid were unavailing, as were attempts to effect Diels-Alder condensations with maleic anhydride, p-benzoquinone, and perfluoroguanidine. The difluorimine was also unreactive in the presence of transition metal ions.

The reaction of n-heptanal with difluoramine in sulfuric acid produced 1, 1-bis(difluoramino)heptane and bis(1-difluoraminoheptyl)ether in amounts that varied with the reaction conditions. Dehydrofluorination of 1,1-bis-(difluoramino)heptane with weak base yielded a product having the composition $C7H_{12}N_2F_2$ instead of the expected trifluoroamidine. Some evidence concerning the structure of the product and a possible mechanism for its formation are presented.

Ethyl N-cyclohexylcarbamate was prepared in 95 percent yield from cyclohexylamine and ethyl chloroformate. Fluorination in aqueous suspension gave cyclohexyldifluoramine and ethyl N-fluoro-N-cyclohexylcarbamate.

SECTION II - SYNTHESIS OF COMPOUNDS FOR STRUCTURE-SENSITIVITY TESTS

A series of organodifluoramines was synthesized for evaluation of the relationship between the structure of these compounds and their sensitivity. The compounds prepared were liquid at room temperature and had carbon-to-NF_2 ratios in the range of 1.7:1 to 4:1. The types of compounds prepared were as follows:

1. Vicinal and geminal bis(difluoramino)cycloalkanes and n-alkanes
2. Vicinal bis(difluoramino)alkyl esters
3. Tris(difluoramino)methoxyalkanes.

Conditions were developed for gas chromatographic purification of the geminal and vicinal bis(difluoramino)alkanes on a preparative scale, and five to 15 gm samples of the purified compounds were sent to the Naval Ordnance Laboratory for sensitivity studies. In the case of tris(difluoramino)methoxyalkanes, a thorough investigation of various gas chromatographic columns and conditions revealed that these compounds cannot be readily purified by this technique.

Gas chromatographic investigations, in conjunction with infrared and NMR spectral analyses, showed that bis(difluoramino)alkyl esters having an NF_2-group on the alpha carbon atom are very sensitive to heat and tend to decompose to the fluorimino derivatives, even on inert columns at temperatures as low as 70°C. Bis(difluoramino)esters in which there are no α-NF_2 groups have significantly higher thermal stability and can be readily purified by gas chromatography.

SECTION III - CHEMISTRY OF THE OXYGEN SUBFLUORIDES

The cubic structure previously reported for O_2AsF_6 from x-ray data has been further substantiated by nuclear diffraction studies. O_2AsF_6 has been found to be soluble and stable in IF_5 at room temperature. Reactions of O_2AsF_6 with NO_2ClO_4, $KClO_4$, BrF_5, $CsClF_4$, $HC(NO_2)_3$, SO_2Cl_2, and $\cdot NF_2$ radicals have been studied. X-ray evidence indicates that a reaction occurs in the solid state between NO_2ClO_4 and O_2AsF_6 to yield NO_2AsF_6 and an unidentified solid phase. The possibility that this solid phase is O_2ClO_4, for which a heat of formation of +6.4 kcal/mole has been calculated, is under study.

Reactions of O_2F_2 with Xe, Cl_2O_7, $ClO.AsF_5$, CsCl, BrF_5, $CsBrF_6$, and $CsClF_4$ have been examined. The reaction of O_2F_2 with Xe below -100°C produces XeF_2 in excellent yields as well as small quantities of unstable oxyfluorides of xenon. The reaction of excess O_2F_2 with $ClO.AsF_5$ gave unidentified liquid and solid products stable at room temperature. Exploratory studies were made of the reactions of O_3F_2 with Cl_2, AsF_5, and NO. No products of interest were obtained in these reactions.

SECTION IV - STABILIZATION OF NITRONIUM PERCHLORATE

Attempts were made to improve the chemical stability of nitronium perchlorate by forming nitronium ion complexes. This approach was unsuccessful because of the general failure of NO_2^+ to form stable complexes. Pyridine was the only molecule found to give a solid complex with NO_2ClO_4. The pyridine complex ($NO_2(py)_xClO_4$) slowly decomposes at room temperature to a brown tar which contains pyridinium perchlorate. Attempts to prepare two new inorganic perchlorates, $H_3NClO_4^+ClO_4^-$ and $H_3NOH^+ClO_4^- \cdot HClO_4$, were unsuccessful.

SECTION V - THERMAL STABILITY OF ADVANCED SOLID OXIDIZERS

The vapor pressure of anhydrous perchloric acid has been studied between 16°C and 60°C. The results are in accord with one previously determined point, but contradict the only other point previously reported. The heat of vaporization has been calculated as 15.03 kcal/mole, giving an extremely high entropy of vaporization of 42.82 e.u./mole at the boiling point at atmospheric pressure (78°C). Thermal decomposition studies at 40°C to 55°C give an activation energy of 22.4-23.1 kcal/mole, in good agreement with Soviet reports.

The thermal decomposition of hydrazinium monoperchlorate was studied between 130°C and 200°C. No decomposition was detected at 130°C for over 100 hours; decomposition between 140°C and 200°C follows a power law relationship during an induction period and a linear law from 10 percent to 80 percent of reaction. Reaction products have been analyzed, a stoichiometry has been proposed, and a mechanism in accord with kinetic and analytical results has been written. The activation energy of the rate-determining step has been calculated as 23.8 kcal/mole, quite close to that obtained for anhydrous perchloric acid.

Preliminary studies on the thermal decomposition of hydroxylammonium perchlorate indicate lower thermal stability than expected on the basis of literature reports. The autocatalytic nature of the reaction is apparent in the P versus t plots at 130°C and 140°C. Mass spectrometric analyses of the gaseous products indicate 80 percent N_2O and 20 percent HCl. No other gaseous products have been detected. Physical characteristics of the residue lead to the supposition that it is largely hydrazinium perchlorate. On this basis, a preliminary stoichiometry and mechanism have been written.

The results of a literature survey of ammonium perchlorate, guanidinium perchlorate, hydrazinium monoperchlorate, hydrazinium diperchlorate, hydroxylammonium perchlorate, and nitronium perchlorate have been presented, and general patterns of similarity among these compounds have been noted.

SECTION VI - CHEMISTRY OF DIFLUORODIAZINE AND NITROSYL FLUORIDE

cis-Difluorodiazine reacts readily with arsenic pentafluoride to yield a white solid adduct stable to above 100°C. The adduct has been characterized as an inorganic diazonium salt, $N_2F^+AsF_6^-$. Some evidence has been obtained that fluorodiazonium tetrafluorochlorate and tetrafluorobromate may be obtained from N_2FAsF_6 by metathesis.

Tetrafluorohydrazine forms an unstable adduct with arsenic pentafluoride from which trans-difluorodiazine, in addition to nitrogen trifluoride may be obtained by thermal decomposition, or, more rapidly, by reaction with nitric oxide. The stoichiometry of the adduct is uncertain, but the present data suggest an N_2F_4:AsF_5 mole ratio between 1:1 and 1.5:1.

A white solid adduct which appears to be a solvated nitrosyl bifluoride, $NO^+HF_2^-\cdot xHF$, is isolable from the liquid $NOF\cdot 3HF$.

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SECTION I

(U)
DIFLUORAMINE CHEMISTRY

Harry F. Smith

Report RMD-5043-64-F

RMD Project 5043, Task 51
Report Period: 1 January 1964 to
31 December 1964

Contract No. NOnr 4364(00)
ARPA Order No. 417
Project Code 4910

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FOREWORD

This section of the final report describes research conducted from 1 January 1964 to 31 December 1964 on the synthesis and chemical reactions of alkyl-difluoramines and related organic nitrogen-fluorine compounds.

The body of this report presents the results of completed studies in the form of preprints of manuscripts prepared for publication. Progress in those research areas in which data is incomplete and/or experimentation is continuing is summarized in the appendix.

Technical personnel contributing to this research effort include H. F. Smith (Project Scientist), A. J. Castellano, and M. J. Socha. Analytical support was provided by R. N. Storey, D. Y. Yee, D. F. Kates, J. A. Creatura, A. W. Fremmer, D. N. Pregler, and D. G. Chowanec.

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I. INTRODUCTION

The objective of this research program was to investigate the chemical properties of alkyldifluoramines and related organic nitrogen-fluorine compounds, and to elucidate the mechanisms of those reactions which are found to occur.

Earlier reports (Ref 1 and 2) have dealt with the reactions of alkyldifluoramines with a variety of reagents, with particular emphasis on oxidizing and reducing agents. Because of the increasing importance of perfluoroguanidine as an intermediate in the synthesis of potential high-energy oxidizers, much of the effort of Thiokol Chemical Corporation, Reaction Motors Division during 1964 was directed toward the study of the reactions of the fluorimino group, $>C{=}NF$ (Ref 3 through 5). We have endeavored to define the scope and generality of addition reactions of active-hydrogen reagents and to determine to what extent the fluorimino group resembles carbonyl and olefinic linkages.

This report presents the results of completed studies on the synthesis and reactions of bis(difluoramino)cyclohexenes and 1,2-difluoriminocyclohexane in the form of a manuscript for publication. Progress in other areas, including the preparation of two model compounds, is described in the appendix.

II. MANUSCRIPT OF PAPER FOR PUBLICATION

The Chemistry of Alkyldifluoramines. III.
The Synthesis and Some Reactions of 1,4-Bis(difluorimino)cyclohexene-2
and 1,2-Difluoriminocyclohexene

Prepared for Submission to
Journal of Organic Chemistry

Contribution from The Chemistry Department, Reaction Motors Division, Thiokol Chemical Corporation, Denville, N.J.

The Chemistry of Alkyldifluoramines. III. The Synthesis and Some Reactions of 1,4-Bis(difluoramino)cyclohexene-2 and 1,2-Difluoriminocyclohexane

Harry F. Smith, Joseph A. Castellano, and Donald D. Perry

1. Preprints of the previous paper in this series were incorporated in Report RMD-AOR-ATS-63.

2. Research reported in this publication was supported by the Advanced Research Projects Agency and administered by the Department of the Navy, Office of Naval Research.

The addition of tetrafluorohydrazine to 1,3-cyclohexadiene produced a mixture of 1,4-bis(difluoramino)cyclohexene-2 and 1,2-bis(difluoramino)-cyclohexene-3. These unsaturated difluoramino compounds decolorized bromine and reacted with acqueous permanganate to yield carboxylic acids. Dehydrofluorination of the difluoramine mixture with a basic ion exchange resin produced the two expected fluorimino compounds. Some photochemical properties of 1,4-difluoriminocyclohexene-2 are discussed.

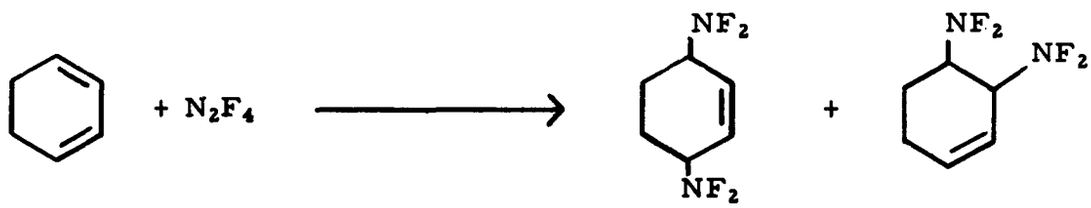
1,2-Difluoriminocyclohexane was synthesized by the addition of tetrafluorohydrazine to cyclohexene, followed by dehydrofluorination of the resulting bis(difluoramine). The difluorimine was hydrolyzed by aqueous sodium hydroxide but did not react with cold concentrated sulfuric acid. Efforts to bring about addition reactions with tetrafluorohydrazine and isocyanic acid were unavailing, as were attempts to effect Diels-Alder condensations of the difluorimine with maleic anhydride, p-benzoquinone. The difluorimine was also unreactive in the presence of transition metal ions.

Exploration of the chemical properties of organic difluoramines properly includes not only transformations of the difluoramino group itself, but also the influences which the group exerts on the reactivity of other functionalities in the molecule. This communication describes some reactions of an olefinic linkage α to difluoramino groups and the photochemical properties of a compound containing a conjugated system which includes two fluorimino groups.

One of the most prominent and general reactions of primary and secondary alkyldifluoramines is the elimination of the atoms of hydrogen fluoride to yield unsaturated products. The alkylidenefluorimines derived from secondary alkyldifluoramines bear a formal resemblance to both olefin and carbonyl functions. This paper describes some experiments directed toward defining the chemical reactivity of a model compound of this class.

Synthesis of Bis(difluoramino)cyclohexenes

The preparation of bis(difluoramino)cyclohexene was accomplished by the addition of tetrafluorohydrazine to 1,3-cyclohexadiene. The thermally initiated reaction proceeded smoothly to give 52 – 62 percent of 1:1 addition product, b.p. 65 – 66° (15 mm), see Table I.



(1)

I II

TABLE I

REACTION OF 1,3-CYCLOHEXADIENE WITH N_2F_4

Diene g. (moles)	N_2F_4 (moles)	Time (hr.)	Temp (°C)	Product g. (moles)	Yield[a] (%)
1.00(0.0125)	0.015	3	80-100	1.77(0.0096)	60.0
3.36(0.0400)[b]	0.06	3	80-100	4.07(0.0221)	52.5
8.0(0.10)[c]	0.12	4	80-100	11.50(0.0625)	62.5
25.0(0.312)[d]	0.32	4	80-100	50.0(0.272)[e]	

a - Based on 1,3-cyclohexadiene
b - Combination of two runs
c - Combination of four runs
d - Combination of 10 runs
e - Crude

The nature of the product was established by means of elemental and infrared analysis (Figure 1). Gas-chromatographic analysis revealed the presence of four components, probably consisting of the cis and trans isomers of I and II (Table II). Definite structural assignments have not been made.

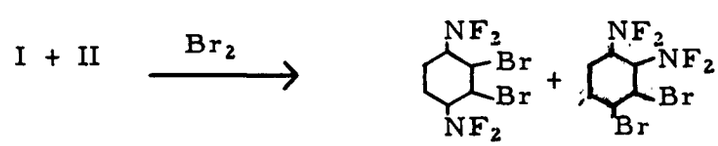
TABLE II

CHROMATOGRAPHIC ANALYSIS OF BIS(DIFLUORAMINO)CYCLOHEXENES

Peak No.	Retention Time (min.)	Weight (%)
1	10.3	24.5
2	12.0	37.0
3	13.75	23.9
4	16.50	14.6

Reactions of the Double Bond

Treatment of a mixture of I and II with bromine in carbon tetrachloride solution resulted in the rapid disappearance of the bromine.



(2)

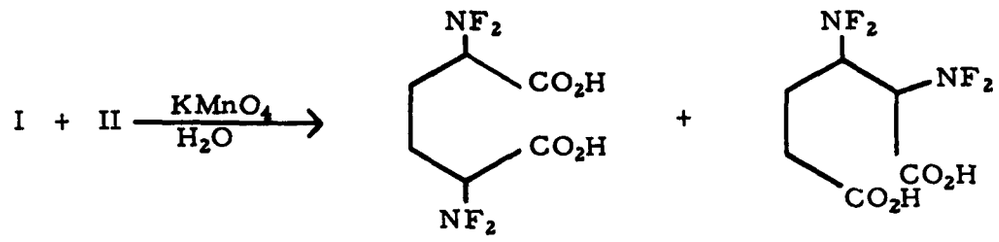
In contrast, bromine did not add to trans-2,5-bis(difluoramino)-2,5-dimethylhexene-3 (III) under identical conditions[3]. This difference in behavior may be

3. Unpublished observations, this laboratory

attributed to steric factors, since electronic influences would be similar in the two cases.

Oxidative cleavage of the double bond is another characteristic reaction of olefins. When a mixture of bis(difluoramino)cyclohexene isomers was treated

with neutral aqueous permanganate a precipitate of manganese dioxide appeared immediately. The complex mixture of liquid organic products which was recovered was shown to contain both carboxyl and N-F groups. Equation 3 indicates the probable cause of reaction. The ability of the difluoramino group to resist



(3)

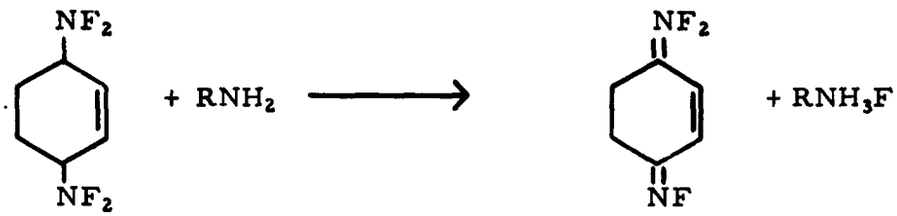
oxidation by permanganate was demonstrated in experiments with trityldifluoramine. The permanganate was not decolorized and the trityldifluoramine was recovered unchanged. The oxidation was less affected by steric factors than was bromination, since III was readily oxidized by permanganate.

Dehydrofluorination of Bis(difluoramino)cyclohexenes

Bis(difluoramino)cyclohexenes differ from the tertiary alkyldifluoramines used as model compounds in earlier studies[1] in that they contain hydrogen atoms in positions α- to the difluoramino groups. These secondary alkyldifluoramines have been found to lose the elements of hydrogen fluoride upon reaction with bases to yield the corresponding alkylidenefluorimines.

Because of the difficulty of separating I and II, increased by the existence of both in cis and trans modifications, mixed bis(difluoramino)cyclohexenes were employed in the dehydrofluorination experiments. A weakly basic ion exhange resin was found to be an effective agent for this purpose. An ether solution of the difluoramines was stirred for four hours with a two-fold excess of a commercial resin (free-amine type) at room temperature. The brown oil which remained after removal of solvent was triturated with pentane, to yield colorless crystals, m.p. 50 – 51°. Elemental analysis of the solid was in excellent agreement with theory for difluoriminocyclohexene. The infrared spectrum (Figure 2) showed strong absorption in the N-F region, as well as sharp peaks at 1580, 1610, and 1630 cm^{-1} indicative of C=N or C=C absorptions. The ultraviolet spectrum showed a strong, broad absorption with a maximum at

239 mμ (ϵ 2 x 10^4). On the basis of these facts, the structure of 1,4-difluoriminocyclohexene-2 (IV) was assigned to the solid product. This assignment was confirmed by the proton magnetic resonance spectrum (Figure 3) which

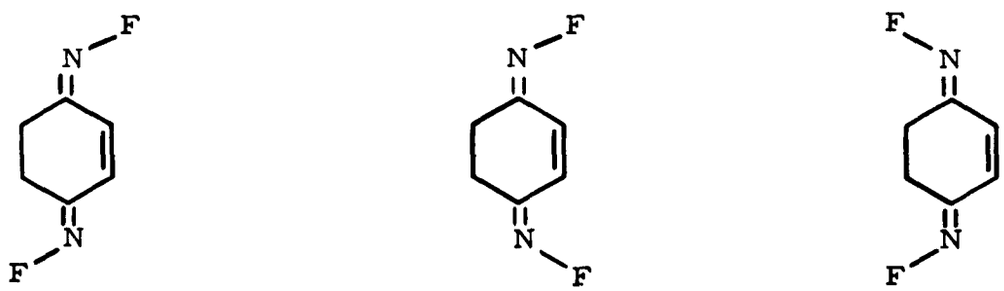


(4)

I IV

where R = polymer residue

consisted of two sharp intense singlets at 174 and 397 c.p.s. downfield from tetramethylsilane. The relative intensities of the two bands were not measured but they appeared to be close to the expected 2:1 ratio; the more intense peaks occurred at higher field strength. Each singlet is superimposed on a complex system, suggesting that a mixture of isomers is present. Three geometric isomers of 1,4-bis(fluorimino)cyclohexene-2 are possible; syn-anti (IVa), syn-syn (IVb), anti-anti (IVc).



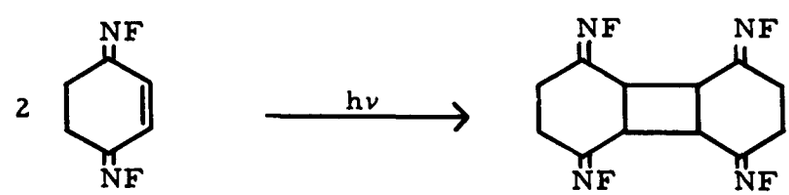
IVa IVb IVc

Distillation of the pentane filtrate remaining after isolation of IV yielded a small quantity of unreacted bis(difluoroamino)cyclohexenes, in addition to some 1,2-difluoriminocyclohexene-3 (V), presumably a mixture of the four possible geometric isomers (Figure 4).

Attempts to effect the dehydrofluorination of mixtures of I and II with other nucleophilic reagents were less successful. The addition of ethanolic potassium hydroxide to the bis(difluoramine) mixture resulted in an exothermic reaction which gave a red, oily product having poorly defined infrared absorptions, and a black insoluble polymer. The reaction of I and II with pyridine yielded a liquid product having an infrared spectrum similar to that shown in Figure 1, but the material darkened and decomposed on standing at -5° and could not be characterized further.

Photochemical Properties of 1,4-Difluoriminocyclohexene-2(IV)

Cyclohexane and acetonitrile solutions of IV exhibit a single broad absorption at 238-240mμ ($\epsilon = 2 \times 10^4$ mole-cm/liter) in the visible-ultraviolet region. On continued exposure the extinction at this wavelength decreased and a shoulder appeared at 272 mμ. Three plausible routes for the photolysis must be considered. The photoinitiated cyclodimerization illustrated in equation 5

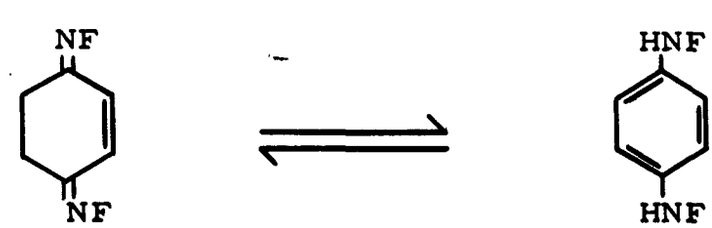


(5)

has been observed with many olefins.[4] Such a process would be

4. A. Mustafa, Chemical Reviews, 51, 1(1952).

expected to cause a diminution in the ultraviolet absorption by destroying the conjugated system involved. Since IV as written is tautomeric with an aromatic structure (equation 6), it is also possible that the absorption of a photon



(6)

leads to a rearrangement of this sort. A third possibility involves the interconversion of two or more of the three geometric isomers depicted above (IVa, IVb, IVc).

Attempts to determine which mechanism is actually involved, by carrying out the photolysis on a preparative scale and isolating the products for identification, were only partially successful. After strong illumination by a mercury-vapor lamp in quartz, the compound absorbing at 272 mμ could not be detected. Only starting material and a black insoluble solid having ill-defined infrared spectrum were found. The same effect was observed, at a lower rate (Figure 5), when the lamp was filtered to provide 50 % cutoff at 240 mμ. These experiments did, however, serve to eliminate the aromatization mechanism from consideration. It is extremely unlikely that an aromatic derivative, if formed, would fail to survive under the experimental conditions, and infrared analysis failed to show any indication of either a substituted benzene or the N-H bond.

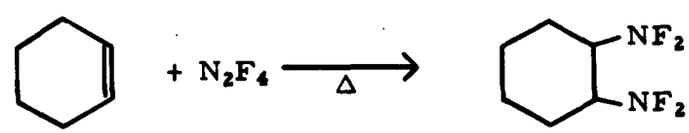
Quantitative photolysis in dilute solution[5] clearly showed the presence of

5. H. Burwasser of these laboratories, results to be published elsewhere.

a shoulder at 272 mμ which increased with continued exposure. The system exhibited two isosbestic points, indicating that a reversible reaction is involved. These observations are best interpreted as a manifestation of the interconversion of geometrical isomers in a ternary system.

Synthesis of 1, 2-Difluoriminocyclohexane (VI)

This difluorimino compound was prepared routinely in a two-step procedure starting with cyclohexene. The thermally initiated addition of tetrafluorohydrazine to the olefin in the gas phase resulted in the formation of 1, 2-bis(difluoramino) cyclohexane (VII). Repeated runs gave a cumulative yield of 55 % of



VII (7)

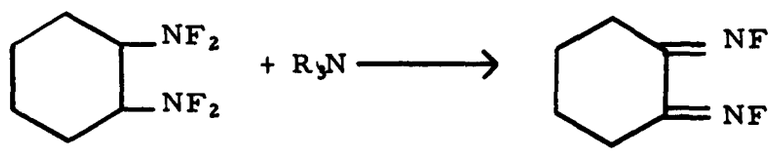
purified product, a mixture of cis and trans isomers. The isomers have been separated by gas-liquid chromatography and identified by means of their infrared, n.m.r., and mass spectra.[6]

6. D. D. Perry, et al, of these laboratories, results to be published.

For the purpose of the dehydrofluorination reaction, however, the isomer mixture was used as obtained. The mixture, dissolved in ether, reacted with suspended basic ion-exchange resin to produce 1,2-difluoriminocyclohexane (VI) in 51 % yield. Ethyldiisopropylamine[7] was also

7. E. A. Lawton and J. A. Weber, J. Am. Chem. Soc., 85, 3595(1963).

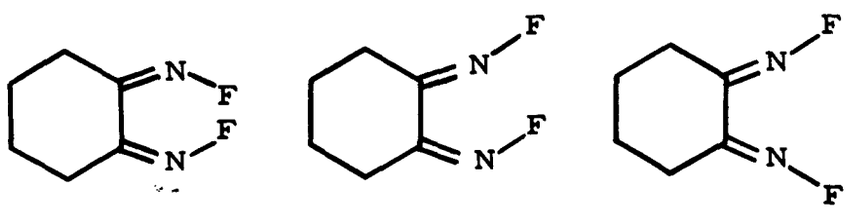
employed successfully in the dehydrofluorination of VII. VI is a colorless liquid, b.p. 68 - 70° (0.22 mm.) and 64 - 66° (0.1 mm.), n_D^{20} 1.4661.



(8)

VII VI

Its infrared spectrum is shown in Figure 6. Geometric isomerism about the C=N bonds makes possible the existence of three isomers, (a) syn-syn, (b) syn-anti, and (c) anti-anti:



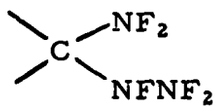
VIa VIb VIc

The relative stabilities and rates of interconversion of the three forms are unknown.

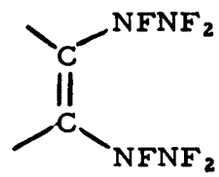
Reactions of 1,2-Difluoriminocyclohexane (VI)

Our investigation of the chemical reactivity of VI has covered several diverse areas. Primarily, efforts were directed toward determining the extent to which the >C=N bond resembles an olefin or a carbonyl. In addition, the stability of VI in the presence of strong acid and base and its ability to form complexes with metal ions were examined.

The addition of tetrafluorohydrazine by a free-radical mechanism to unsaturated sites is a known reaction of considerable generality. Many 1,2-bis-(difluoramino) alkanes and 1,4-bis(difluoramino) alkenes have been produced in this way. If a similar addition occurred at the double bonds in VI, interesting new structures of the types



and



would be obtained. When mixtures of VI and tetrafluorohydrazine were heated at subatmospheric or at elevated pressures, however, the reagents were recovered unchanged.

Attempts to bring about the addition of isocyanic acid to VI have also been unavailing. Isocyanic acid, generated by the pyrolysis of cyanuric acid,[8] was

8. G. Brauer, Handbook of Preparative Inorganic Chemistry, I, (1963).

condensed under vacuum into a bulb containing VI. The temperature was increased in stages, culminating in a 16-hr. period at 25 - 28°. The acid was found to have reverted to the trimer and VI was recovered. This negative result is in contrast to the reported addition of isocyanic acid to both carbonyl groups[9] and olefinic linkages.[10]

9. F. W. Hoover, H. B. Stevenson, and H. S. Rothrock, J. Org. Chem., 28 1825(1963).

10. F. W. Hoover and H. S. Rothrock, ibid., 29, 143(1964).

The formal resemblance of VI to a conjugated diene suggests that it might participate in a Diels-Alder reaction. Accordingly, a sample was heated with maleic anhydride, a relatively reactive dienophile. The volatile liquid product showed infrared absorptions corresponding to both N-F and anhydride groups, but elemental analysis revealed that two moles of difluorimine were present per mole of anhydride. The product was separated by gas-liquid chromatography into the two starting materials and proved to be an azeotropic mixture rather than a true adduct. VI similarly failed to react with either p-benzophenone or tetracyanoethylene, the most reactive dienophile known.[11] In the latter case the

11. T. L. Cairns, et al, J. Am. Chem. Soc., 80, 2775(1958).

reagents were heated to the point of decomposition without any indication that a Diels-Alder product was formed.

A small quantity of VI was mixed with an excess of 50 % of sulfuric acid and stirred at room temperature. After 20 hr. the mixture was worked up and the difluorimine was recovered unchanged. No other organic products could be detected. The fluorimino group is therefore inert to attack by a strong electrophile. This is in contrast to the behavior of alkyldifluoramines, which are protonated and then eliminate either hydrogen fluoride or difluoramine under these conditions.[12, 13]

12. H. F. Smith and D. D. Perry, The Chemistry of Alkyldifluoramines. II. Reaction with Nitric Acid. To be published.

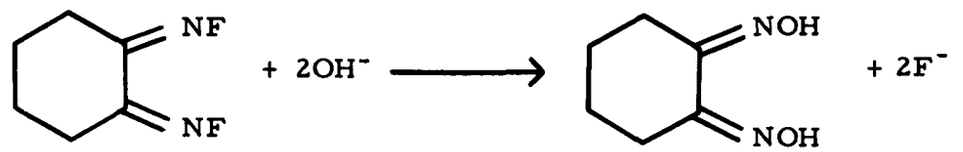
13. W. H. Graham and C. O. Parker, J. Org. Chem., 28, 850(1963).

Stability toward strong base is an important consideration in the synthesis of alkylidenefluorimes and in their possible utilization in further syntheses. In preliminary experiments it was observed that aqueous sodium hydroxide was consumed by VI. On a larger scale the fluorimine appeared to react rapidly with 0.5 N sodium hydroxide forming a homogeneous solution. Titration of the mixture after 48 hr. produced the curve shown in Figure 7. The first inflection at pH 7.25 was probably due to unreacted sodium hydroxide and the second at pH 5.30 may be attributed to a carboxylic acid salt. According to this interpretation, 85 % hydrolysis occurred, producing a 30% yield of carboxylate. The color of the reaction mixture precluded a reliable determination of the amount of fluoride ion produced. Any organic products formed were sufficiently hydrophilic to prevent extraction with ether.

One possible interpretation of the observed results involves mucleophilic attack on nitrogen and simultaneous or subsequent displacement of fluoride ion. A base-catalyzed hydrolysis of the dioxime (VIII) would probably ensue, yielding cyclohexandione (IX). IX is subject to further nucleophilic attack[14],

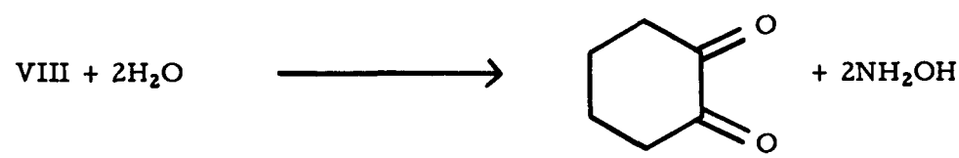
14. A. I. Vogel, A Textbook of Practical Organic Chemistry, Longmans, Green and Co., 974(1948).

undergoing a benzilic type rearrangement with ring contraction to give a hydroxyacid salt (X) as the final product.



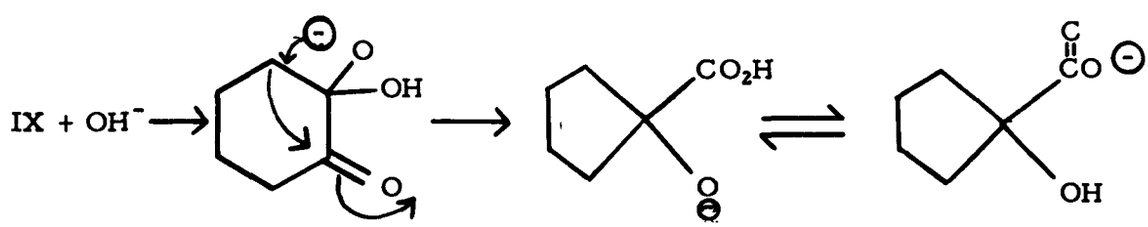
(9)

VI VIII



(10)

IX



(11)

X

It is also possible that some of the sensitive diketone (IX) was oxidized by air to adipic acid. Other possible reaction courses, including initial nucleophilic attack on carbon, cannot be ruled out completely.

The geometric arrangement of a structure like VI suggests the possibility that bidentate coordination complexes with metal ions might be formed. It was found, however, that no precipitation or color changes occurred when an alcoholic solution of VI was added to aqueous solutions of ferric, cobalt, nickel, or cupric salts. This failure to form coordination complexes may be due to the strongly electronegative fluorine substituents, or to the steric complications introduced by the possible existence of syn or anti configuration at each double bond.

EXPERIMENTAL

Reaction of N_2F_4 with 1,3-Cyclohexadiene - A 2-l. Pyrex bulb was charged with 1.0 g. (12 mmoles) of 1,3-cyclohexadiene under a stream of nitrogen. The liquid was cooled to -78° and the bulb evacuated. After degassing several times, 15 mmoles of N_2F_4 was condensed into the bulb at -196° and the bulb heated at 80 - 100° for 3 hr. At the end of this time, practically all of the N_2F_4 had been consumed and the liquid was distilled from the bulb into a -78° trap. The crude product, 1.77 g. was distilled to yield 1.38 g. (60% bis-(difluoramino)cyclohexene isomer mixture, b.p. 65-68° (12.5 mm.).

Anal. Calcd. for $C_8H_8N_2F_4$: C, 39.14; H, 4.38; N, 15.21; F, 41.27
Found : C, 38.84; H, 4.42; N, 15.26; F, 41.48. (by diff).

The product was chromatographed with the Aerograph A-90-P using a 5-ft. column containing 20% SF 96 silicone oil on firebrick. The operating conditions of the instrument were as follows:

injector temp:	180°	attenuation :	1 X
column temp :	115°	sample size:	1 μl.
detector temp:	225°	He flowrate :	59 ml./min.

The area under each peak was measured with a planimeter.

Reaction of Bis(difluoramino)cyclohexene with Permanganate - Addition of 40 ml. 0.1N $KMnO_4$ solution to three drops of bis(difluoramino)cyclohexene (mixture of 1,2- and 1,4- isomers) gave immediately a brown precipitate of MnO_2. The mixture was extracted with CH_2Cl_2, the extract dried, and the solvent evaporated to yield a liquid product. The infrared spectrum indicated the presence of COOH and NF.

Reaction of Bis(difluoramino)cyclohexene with Bromine - Two drops of a solution of bromine in carbon tetrachloride were added to two drops of bis-(fluorimino)cyclohexene (isomer mixture). The bromine color disappeared on standing for 4 hr. at room temperature. Trityldifluoroamine has not decolorized bromine after 48 hr. at room temperature.

Dehydrofluorination of I and II - A solution of 1.84 g. (10 mmoles) of a mixture of I and II in 20 ml. ether was stirred with 8.0 g. (40 mmoles) of weak base ion exchange resin (Amberlite IR-45, 5.0 meq/gm for four hours at room temperature. The solution became deep red and the resin turned black. The resin was filtered and washed with ether, the ether washings being added to the filtrate. The solution was evaporated to dryness to give 1.0 g. of brown oil, which was crystallized from pentane to yield 0.15 g. (10.5%) of colorless crystals, m.p. 50 - 51°.

Anal. Calcd. for $C_6H_6N_2F_2$: C, 50.00; H, 4.20; N, 19.44; F, 26.36.
Found : C, 48.98; H, 4.31; N, 19.45; F, 26.40.

The ultraviolet spectrum of the product was recorded with a Beckman DK-2 spectrophotometer. The maximum absorption occurred at 239 mμ with an extinction of approximately 20,000. The proton magnetic resonance spectrum was obtained with a Varian Associates DP-60 spectrometer. The sample was prepared in $CFCl_3$ solution containing 1 - 2% tetramethylsilane as an internal reference. The solid product was chromatographed with the Aerograph A-90-P using a 5-ft. column containing 20% SF 96 silicone oil on firebrick. The operating conditions of the instrument were as follows:

injection temp:	180°	attenuation :	1 X
column temp :	160°	sample size:	2 μl. of 50% solution in CH_2Cl_2
detector temp:	260°	He flowrate :	50 ml./min.

Under these conditions, peaks appeared at 10.75 and 13.5 minutes retention time.

The pentane filtrate was distilled to yield V, a yellow liquid, b.p. 103-105° (11 mm), m.p. 15-17°.

Anal. Calcd. for $C_6H_6N_2F_2$: C, 50.00; H, 4.20; N, 19.44
Found : C, 49.97; H, 4.26; N, 19.38.

The infrared spectrum of V was indistinguishable from that of its isomer IV.

Photolysis of 1,4-Difluoriminocyclohexene-2

(1) A cylindrical Pyrex reactor was fabricated to fit around a water-cooled quartz immersion well containing a 450-watt, high-pressure, mercury arc lamp (Hanovia No. 679 A-36). An annular space of 1 mm. width was left between the well and the wall of the reactor. The reactor with well in place held 60 ml. of liquid, about 1/3 of which was exposed to the direct rays of the lamp. A solution of 0.72 g. (5 mmoles) of IV in 65 ml. reagent grade cyclohexane was prepared, and 5 ml. was retained as a spectrophotometric reference. Upon irradiation of the remaining 60 ml. at 20°, a distinct discoloration was apparent after 5 - 10 min. The solution became yellow and a brown solid was deposited on the walls of the quartz well. Five brief exposures were given with intermittent mixing. Evaporation of the filtered cyclohexane solution gave a pasty solid from which colorless crystals of starting material were obtained by trituration with pentane. The brown-black insoluble solid gave an indistinct infrared spectrum containing N-F absorptions.

(2) A larger reactor of similar design, providing a solution thickness of ca. 1 cm. to allow more rapid mixing of the exposed portion of the solution, was prepared. A cyclohexane solution of IV was irradiated as above, except that the light source was screened by a Vycor filter (50% cutoff) at 240 mμ. Aliquots were taken at intervals for measurement of ultraviolet absorption curves. The end products were the same as described above.

1,2-Bis(difluoramino)cyclohexane (VII) - Tetrafluorohydrazine (3.12 g. 30 mmoles, measured by volume assuming ideality) was condensed into an evacuated 2-l. bulb containint 2.18 g. (27 mmoles) of cyclohexene (Eastman, "White Label"), and the bulb was then heated in an enclosing mantle at 100 ± 5° for 5 hr. After cooling to room temperature the bulb was attached to a vacuum line and the contents were distilled under vacuum into a trap cooled to -78° in order to remove unreacted N_2F_4. The crude products obtained from six similar experiments was combined and distilled, b.p. 69-82° (27.5 mm.), $n_D^{27.5}$ 1.4107. A yield of 16.2 g. (55%) was obtained.

Anal. Calcd. for $C_6H_{10}N_2F_4$: C, 38.71; H, 5.41; N, 15.05; F, 40.83
Found : C, 38.70; H, 5.61; N, 14.86; F, 40.63

1,2-Bis(fluorimino)cyclohexane (VI)

(1) 1,2-Bis(difluoramino)cyclohexane (16 g., 86 mmoles) was dissolved in 100 ml. ethyl ether. To this solution was added 64 g. (240 meq.) Amberlite IR 45 and the mixture was stirred at 30° under a nitrogen atmosphere for 24 hr.

The spent resin was then removed by filtration and washed with ether. The filtrate and washings were comined, dried, and evaporated to dryness. The residue, a yellow liquid (9.3 g.), was distilled b.p. 68-70° (0.2 mm.) 64-66° (0.1 mm.) to yield 6.3 g. (50%) of pure product, m.p. 5-6°, (n_D^{20} 1.4661).

Anal. Calcd. for $C_6H_8N_2F_2$: C, 49.31; H, 5.52; N, 19.7; F, 26.00
Found : C, 49.53; H, 5.51; N, 18.97, F, 25.99 (by difference)

MW. Calcd: 146.14 Found: 146/152

(2) A mixture of 1.0 g. (5.4 mmoles) of 1,2-bis(difluoramino)cyclohexane, 1.4 g. (10.8 mmoles) of ethyldiisopropylamine (Ref 13) and 25 ml. ethyl ether was refluxed for 20 hr. A viscous brown oil had separated out at the end of this time. The mixture was treated with water and the aqueous solution extracted with ether. The combined ether extracts were dried over magnesium sulfate and evaporated to dryness to yield 0.65 g. (83%)of yellow liquid. The infrared spectrum of this product was practically identical to that of pure 1,2-difluoraminocyclohexene.

Attempted Reaction of VI with N_2F_4

(1) A 500-ml. bulb was charged with 0.70 g. (5 mmoles) of VI, and degassed at -195°. N_2F_4 (0.73 g., 7 mmoles) was introduced and the bulb was heated to 80 - 100° for 5 hr. Upon cooling there was recovered 0.45 g. of brown liquid which was shown by infrared analysis to be impure VI.

(2) A solution of 1.46 g. (10 mmoles) of VI in 15 ml. of Freon-113 was placed in a 75-ml. Hoke cylinder. N_2F_4 (60 mmole) was condensed in and the reactor was heated to 80° for 12 hr. Calculated pressure was 310 p.s.i., based on N_2F_4. After cooling, 92% of the VI was recovered.

Attempted Reaction of VI with Isocyanic Acid - A Vycor tube (52.5 x 1.13 cm.) was charged with 2.6 g. (20 mmole) of cyanuric acid. The tube was placed in a Sargent Micro Combustion Apparatus and the outlet was connected, by means of a ball joint, to a trap maintained at -78°. A stream of dry N_2 was placed through the tube and the ovens were turned on. Both ovens were maintained at 500 - 600° for 30 min. The isocyanic acid which collected in the 78° trap was purified by trap-to-trap distillation in a vacuum system. The pure isocyanic acid was then condensed into a 2-l. bulb containing 1.46 g. (10 mmole) of 1,2-difluoriminocyclohexane. The mixture was held at -196°

for 20 min. and then at -78° for 1 hr. When the cooling bath was removed a clear homogeneous liquid phase was present in the trap but as the mixture warmed to room temperature a white solid formed. After standing overnight at room temperature, the bulb was found to contain no gas. Most of the white solid was insoluble in CCl_4 and CH_2Cl_2. Infrared analysis of the liquid residue from the organic solution showed it to be the starting fluorimino compound and the white solid was identified as cyanuric acid.

Attempted Reaction of VI with Maleic Anhydride

(1) Maleic anhydride was recrystallized from chloroform, m.p. 51-52°, and 0.98 g. (10 mmoles) was dissolved in 5.0 ml. of benzene. This solution was added to 1.46 g. (10 mmoles) of 1,2-difluoriminocyclohexane and the mixture was refluxed for 2.5 hr. At the end of this time, the benzene was removed by evaporation and the residual oil taken up in hot $CHCl_3$-pentane. The crystals which separated on cooling the solution were filtered to yield 0.80 g. (80%) of pure maleic anhydride.

(2) The unreacted starting material recovered from (1) above, was recombined and refluxed with 2 ml. of xylene for 8 hr. At the end of this time, a black precipitate had formed. The mixture was filtered and the filtrate concentrated *in vacuo*. The residue from the filtrate was distilled to yield 0.64 g. of colorless liquid, b.p. 58 - 60° (0.15 mm.). The infrared spectrum of the liquid exhibited absorptions indicative of both the fluorimine and maleic anhydride. Gas chromatography on a 6-ft. stainless steel column packed with 20% SF 96 silicone oil in firebrick at 185° showed peaks at relative retention times of 1.00 min. and 4.50 min. which correspond to maleic anhydride and 1,2-bis(fluorimino)cyclohexane respectively. The infrared spectrum of the black solid showed absorption for OH, CH, and CO but none for N-F. This material is believed to be a polymeric product.

Attempted Reaction of VI with *p*-Benzoquinone - A mixture of 1.46 g. (10 mmoles) of 1,2-difluoriminocyclohexene, 0.57 g. (5 mmoles) of *p*-benzoquinone, and 10 ml. of toluene was refluxed for 48 hr. At the end of this time, the toluene was removed by evaporation and the mixture of starting materials (infrared spectrum) was heated at 200° for 2 hr. The resulting black solid, 1.25 g., was largely decomposed matter.

Attempted Reaction of VI with Tetracyanoethylene - Under an atmosphere of dry nitrogen 1.28 g. (10 mmole) of tetracyanoethylene (DuPont) was dissolved in 15 ml. of dry CH_2Cl_2. This solution was mixed with a solution of 1.46 g. VI (10 mmole) in 10 ml. of CH_2Cl_2; there was no detectable exotherm. The solvent was distilled off and the residue was heated on a steam bath for eight hr. The infrared spectrum of the dark brown pasty solid product showed absorptions due to N-F and C≡N, but no bands that could not be attributed to one or the other of the reactants. The mixture was further heated to 180° for 7 hr. The product was a brown-like glassy solid, only partially soluble in acetone. Its infrared spectrum showed no N-F and only weak C≡N absorptions, indicating that extensive decomposition had occurred. There was no indication that a Diels-Alder adduct has formed.

Reaction of VI with Sodium Hydroxide

(1) A mixture of 1.46 g. (10 mmole) of 1,2-bis(fluorimino)cyclohexane and 50.00 ml. of 0.4995 N sodium hydroxide solution was stirred at room temperature for 48 hr. The color changed from pale yellow to red during the first 30 min. and the mixture became homogeneous. The mixture was titrated potentiometrically with 0.4321 N HCl and was found to have inflections at pH of 7.25 (5.185 meq.) and 5.30 (8.210 meq.). Thus 19.80 meq. of sodium hydroxide was consumed in the reaction, 3.025 meq. being used to form the salt of a carboxylic acid. The acidified solution (pH 2.0) was extracted with ether and CH_2Cl_2. The combined organic extract was dried over sodium sulfate and evaporated to dryness to yield only a small amount of Kel-F grease. The aqueous solution was found to contain 420 mg. (113%) of fluoride ion.

(2) A mixture of 0.2 g. of 1,2-bis(fluorimino)cyclohexane and 12.00 ml. of 0.500 N sodium hydroxide solution was stirred at 40° for 24 hr. The color changed from pale yellow to orange and the mixture became homogeneous. The solution was titrated with 0.4921 N hydrochloric acid solution to the phenolphthalein end point was found to require 6.0 ml. The acidified solution was extracted with ether and methylene chloride as before but only Kel-F grease was obtained. The solution was diluted to 250 ml. and was found to contain 46.3 mg. (90%) of fluoride ion.

Acknowledgement - The authors wish to thank Mr. Richard L. Hanson of the Office of Naval Research and Dr. Murray S. Cohen of these laboratories for their interest and encouragement during the course of this work. Analytical assistance by D. G. Chowanec, J. A. Creatura, A. W. Fremmer, D. F. Kates, D. N. Pregler, R. N. Storey, and D. Y. Yee is gratefully acknowledged.

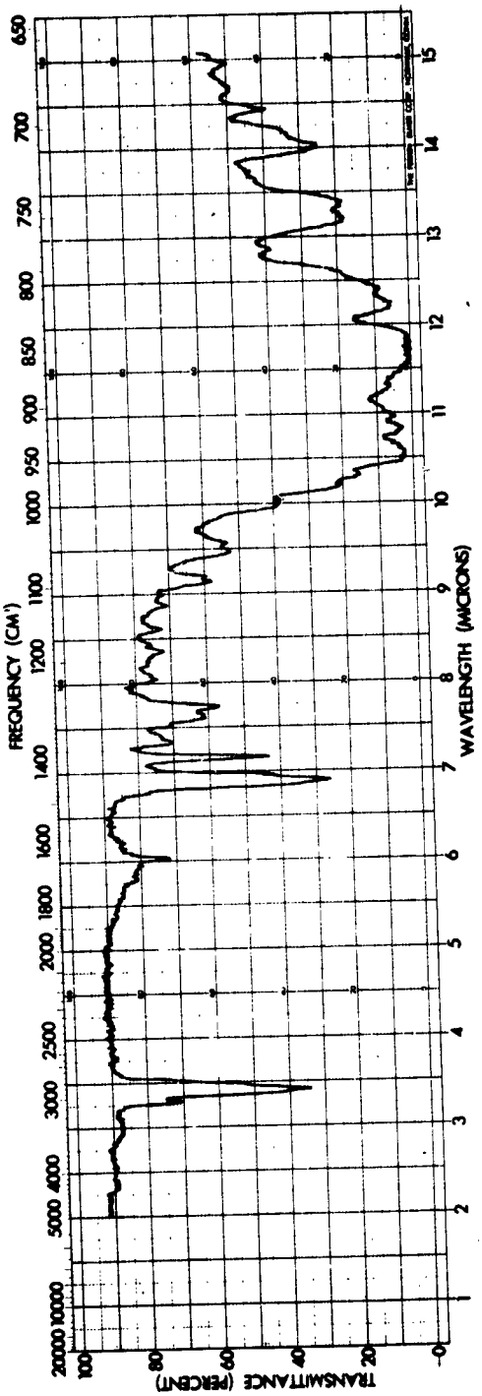


Figure 1. Infrared Spectrum of Bis(difluoramino)cyclohexene Isomer Mixture

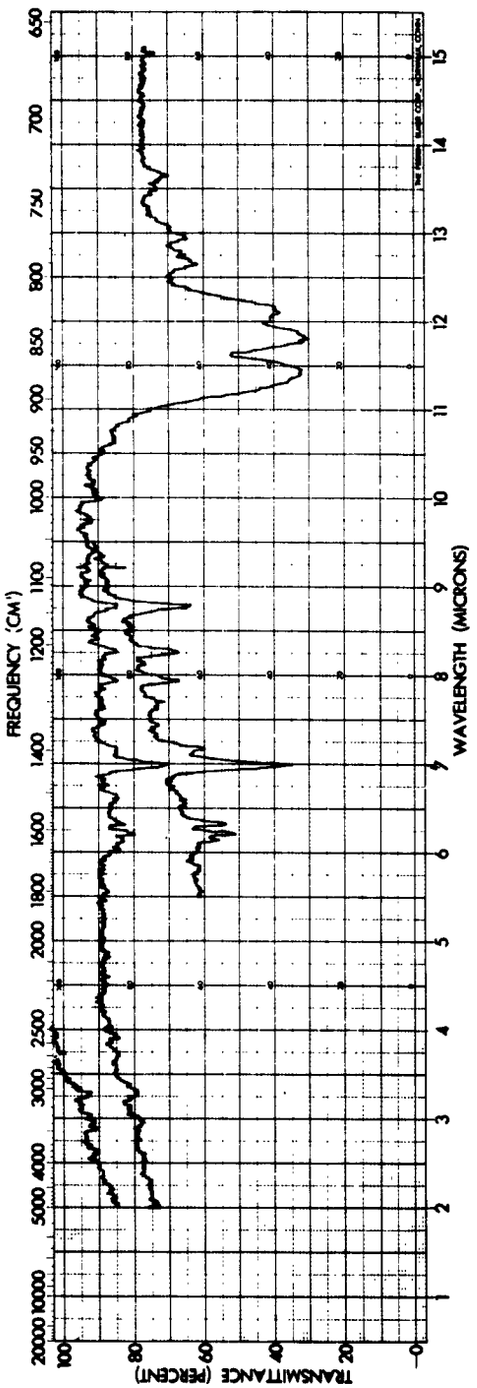


Figure 2. Infrared Spectrum of 1, 4-Difluoriminocyclohexene-2

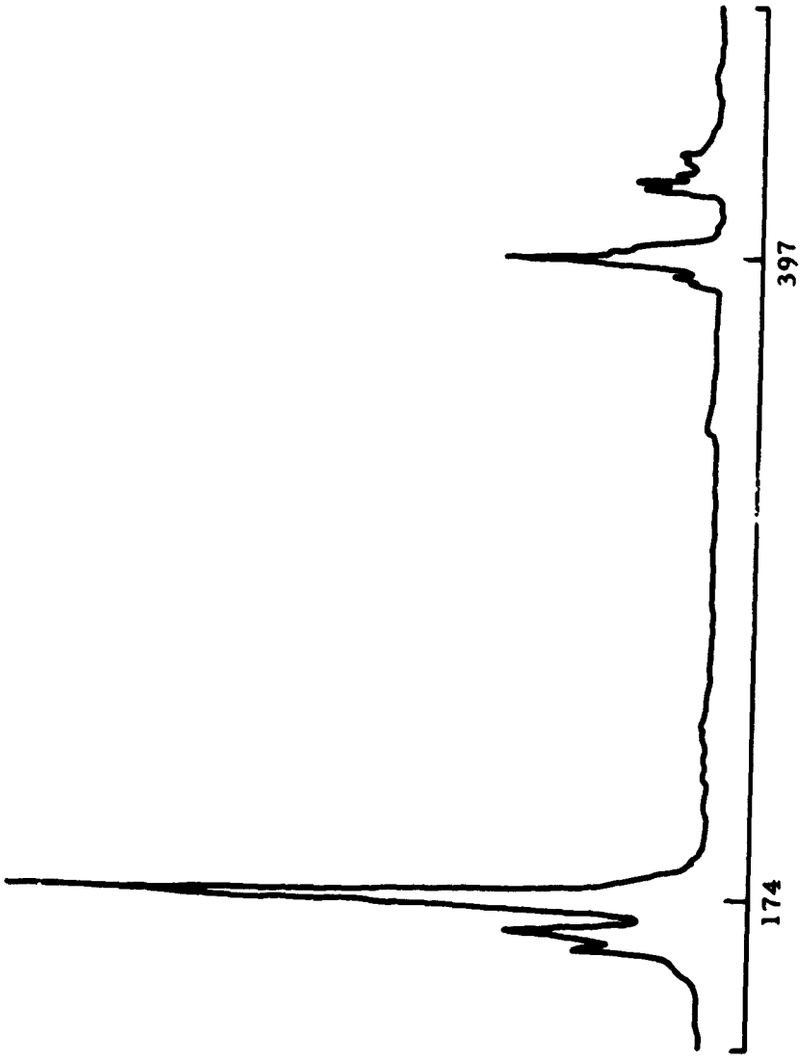


Figure 3. Proton Resonance Spectrum of 1, 4-Difluoriminocyclohexene-2

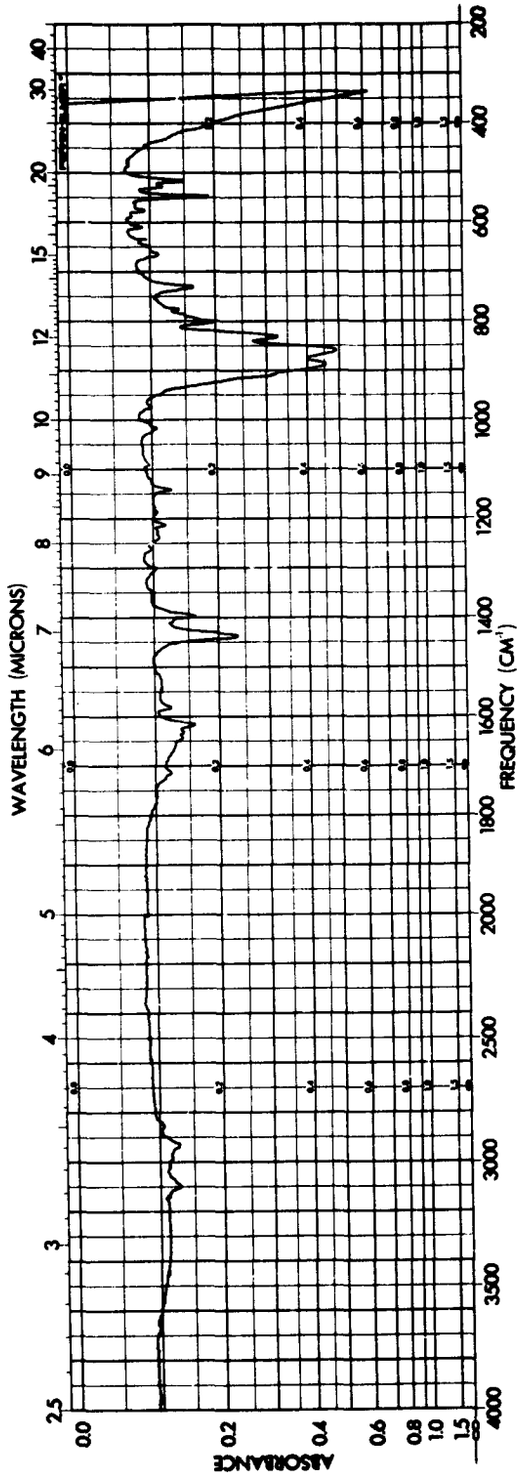


Figure 4. Infrared Spectrum of 1, 2-Difluoriminocyclohexene-3

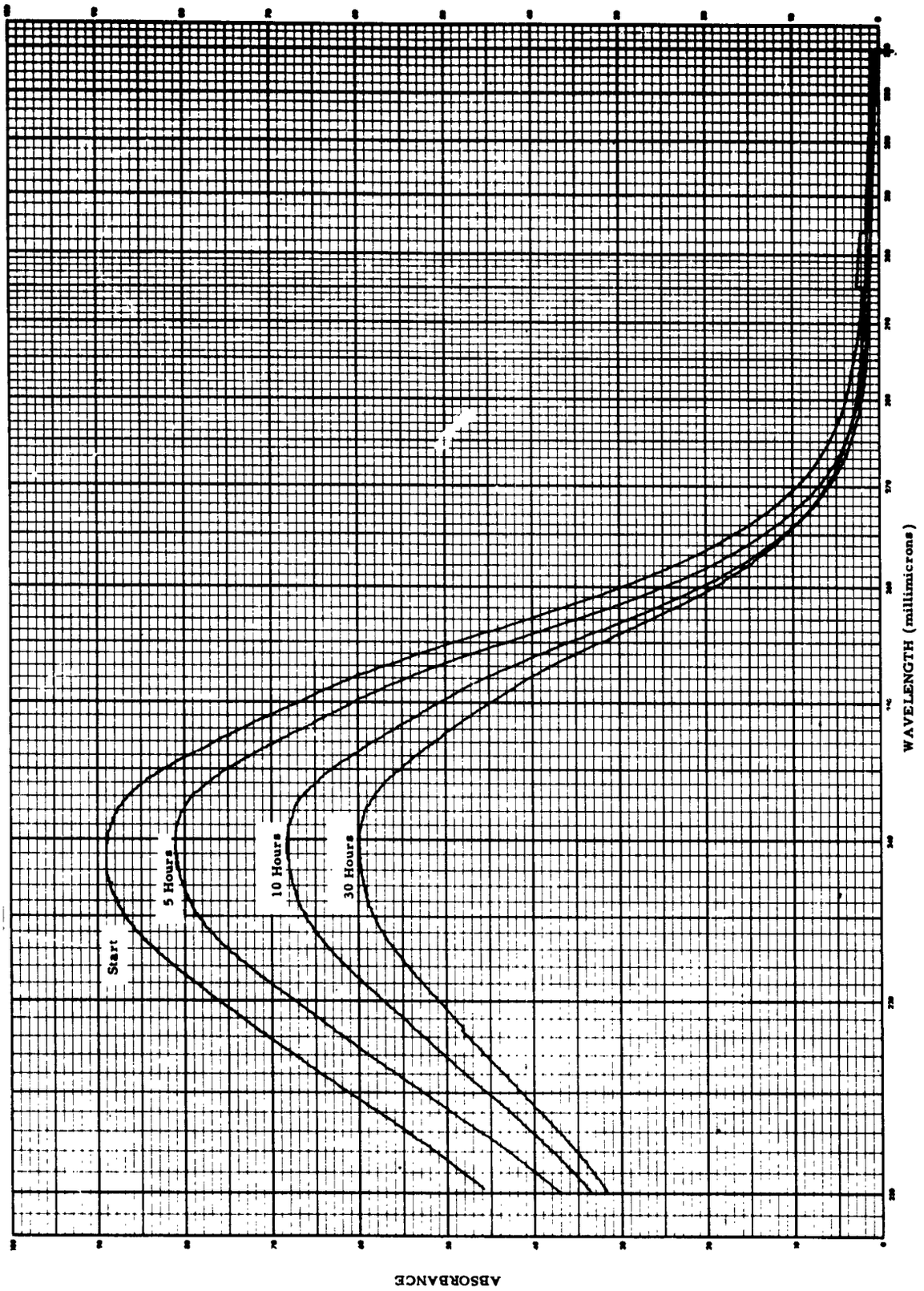


Figure 5. Changes in Ultraviolet Absorption Spectrum of 1,4-Difluoriminocyclohexene-2 During Photolysis

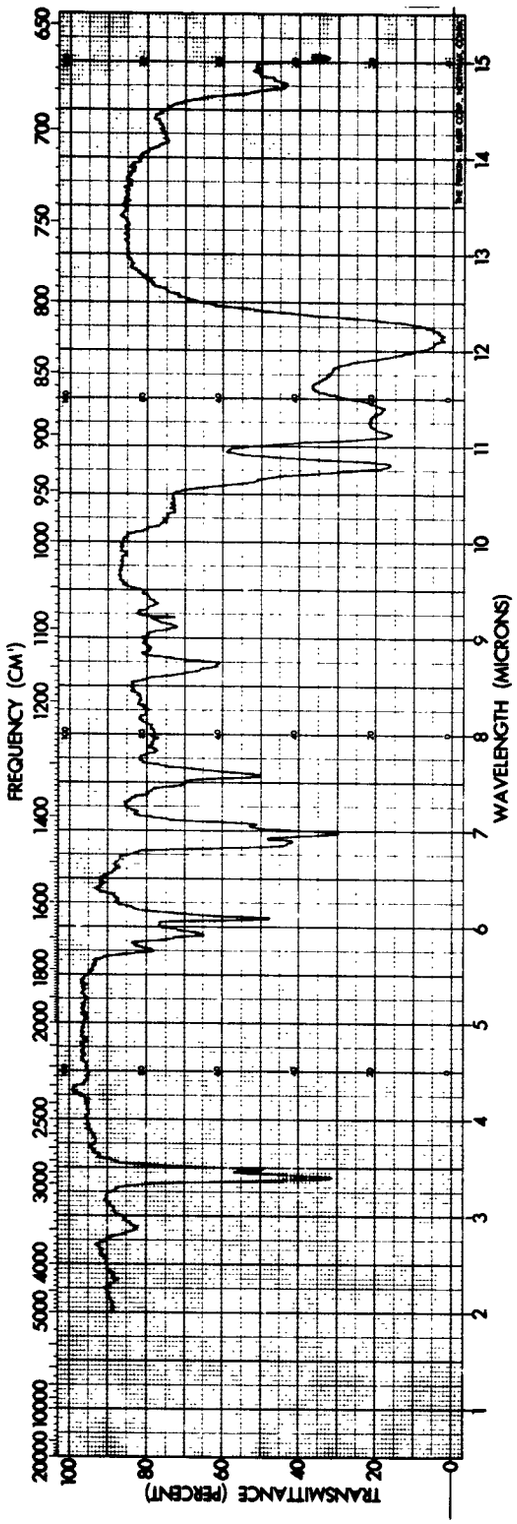


Figure 6. Infrared Spectrum of 1, 2-Difluoriminocyclohexane

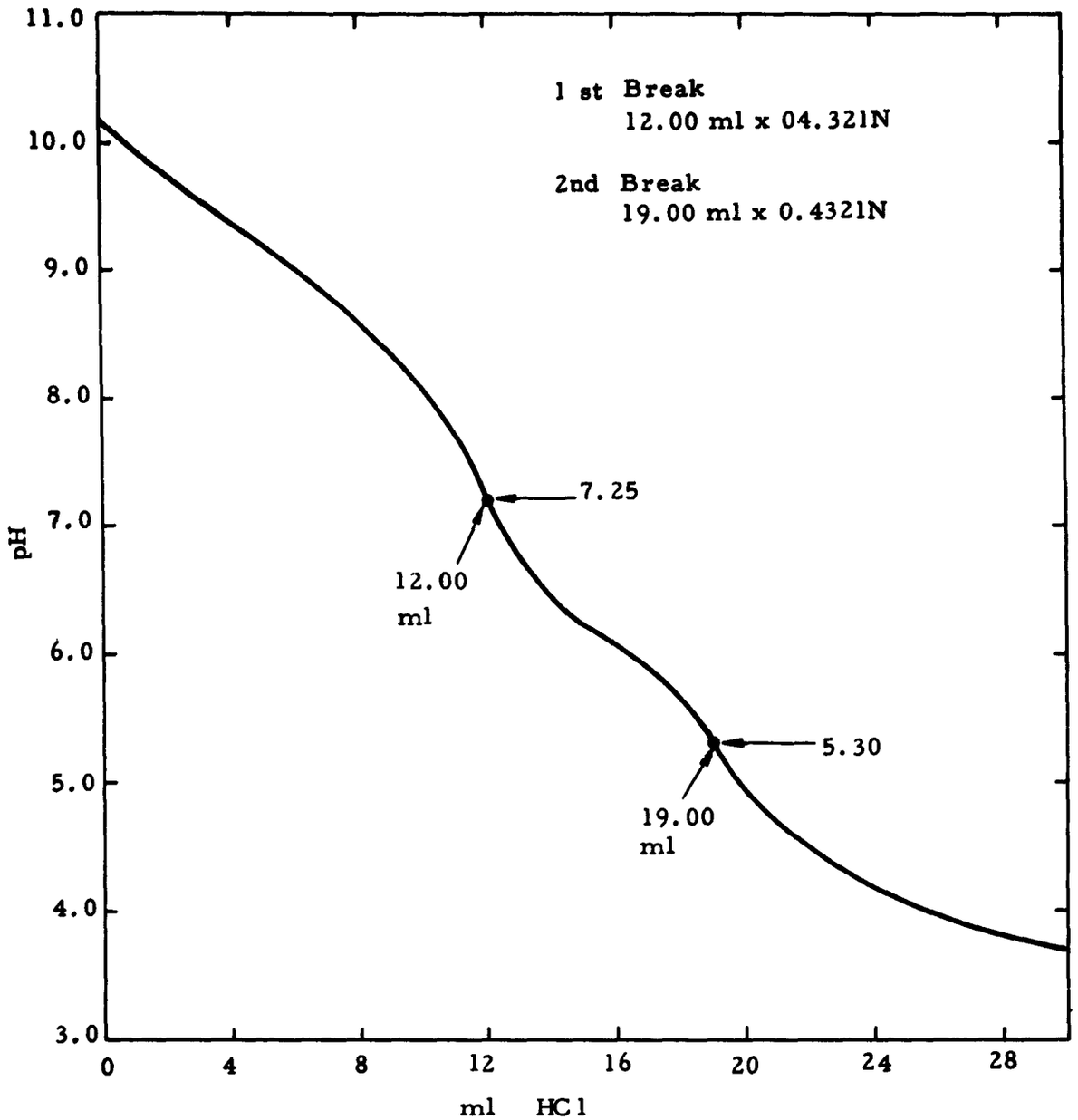


Figure 7. Titration Curve, Reaction of 1, 2-Difluoriminocyclohexane with Sodium Hydroxide

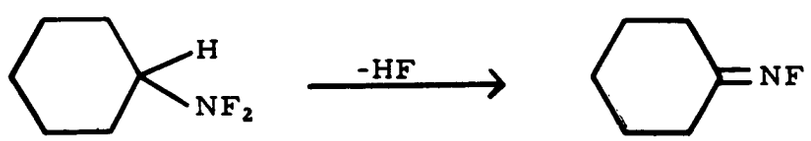
III. APPENDIX - DIFLUORAMINE CHEMISTRY

A. DISCUSSION

This research program on the chemical properties of organic N-F compounds has continued to be directed toward an exploration of the reactivity of the fluorimino group during the past year. Studies completed so far on the chemical reactions of 1, 2-difluoriminocyclohexane indicate the need for extension in two directions. First, a simpler model compound is required for better understanding of some of the effects observed. Both electronic and steric factors introduced by the presence of two fluorimino groups on adjacent carbon atoms may complicate the system. Cyclohexylidenefluorimine (I) should serve admirably, avoiding these complications and having the added advantages of being non-shock sensitive and sufficiently high in molecular weight to facilitate handling of both reactant and potential products. Secondly, the original justification for initiating a study of alkylidenefluorimines rested, at least in part, upon analogy to known addition reactions of perfluoroguanidine. Since none of these reactions occurred with 1, 2-difluoriminocyclohexane, RMD's studies are now being extended to include fluorimines which contain more strongly electronegative substituents, and thus are more closely analogous to perfluoroguanidine. The first compound in this category to be examined is N, N, N'-trifluoroheptylamidine.

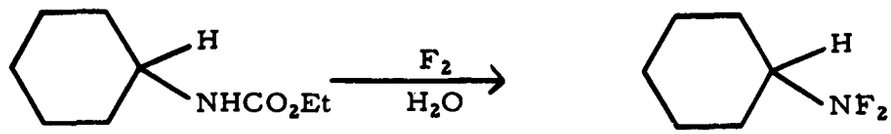
1. Synthesis of Cyclohexyldifluoramine (II)

The obvious synthetic approach to I involves the dehydrofluorination of difluoraminocyclohexane (II). The preparation of the required difluoramine



II I (1)

by aqueous fluorination of ethyl N-cyclohexylcarbamate (III) has been described (Ref 6). The carbamate, although no longer available commercially, is



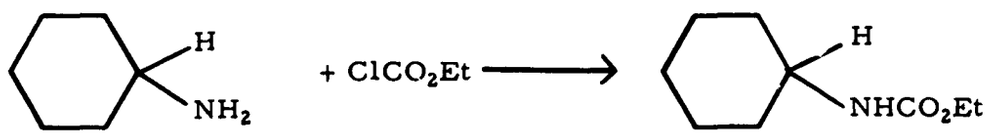
(2)

III II

obtainable by either of two routes.

(3)

III



(4)

III

The method shown in equation 4, based on a published synthesis of the analogous benzyl compound (Ref 7), was chosen for this work and has proven to be highly successful. On a one-mole scale, the reaction of cyclohexylamine with ethyl chloroformate in the presence of sodium hydroxide produced the carbamate in 95.5% yield, m.p. 52 - 54.5° (lit. 56°, Ref 5; 56 - 58°, Ref 6). material was used in the next step of the synthesis sequence without further purification.

A suspension of III in water was treated with a 10% excess of nitrogen-diluted fluorine at <10°. The product was extracted with methylene chloride,

dried, stripped of solvent, and distilled. Although the fractionation was not very efficient, it was ascertained that approximate yields of 8-9% II and 5-6% ethyl N-fluoro-N-cyclohexylcarbamate (IV) were obtained. Approximately 73% of III was recovered. Identification of the products was accomplished by infrared and n.m.r. analyses.

It was observed during the experiment just described that the carbamate was remarkably hydrophobic, and even after being dispersed tended to float on top of the water. When the fluorination was repeated, a small quantity of a nonionic surfactant was included, and a more complete dispersion was obtained. In addition, the excess of fluorine used was increased from 10% to 150% in a further effort to drive the reaction to completion. The liquid product was extracted and worked up as before.

The yields of fluorinated products were still low (5% II and 11% IV). The recovery of III decreased, as compared with the earlier run, suggesting that some of the volatile product (II), was lost during the fluorination. Collection of the stripped solvent and examination v.p.c. revealed that no significant amount of product was lost during the solvent removal.

As in the first preparation, fractional distillation failed to provide an efficient separation of the several components. Reported (Ref 6) boiling points are 36 - 42° (25 mm.) for II and 49 - 52° (0.1 - 0.2 mm.) for IV. The first distillation fraction, taken at 25 - 35 ^{o} (26 - 27 mm.) and believed to be residual solvent, was found by infrared analysis to be principally II and with a small amount of IV. V.p.c. (Figure 1) revealed the presence of additional impurities in trace quantities. The second distillation fraction, 37 - 41° (26 - 27 mm.) Figure 2, contained a slightly higher proportion of IV. A small amount of II remained to contaminate the IV collected at 41 - 70° (0.10 - 0.12 mm.), Figure 3.

Preparative scale v.p.c. of fraction I (Figure 4) gave a pure sample of II for infrared (Figure 5) and n.m.r. (Figures 6 and 7) analysis, and a sample of IV containing traces of II. (Infrared curve is shown in Figure 8.)

2. Dehydrofluorination of Cyclohexyldifluoramine (II)

The first two distillation fractions of the product from the first fluorination, which were rich in II, were combined and treated at room temperature with an ether suspension of a basic ion-exchange resin. The infrared spectrum of the product showed no significant changes as compared to that of the starting material. The F^{19} n.m.r. spectrum showed only II (a doublet centered at -41.74 p.p.m. from $CFCl_3$, H-F coupling constant 19.1 cycles). Chromatographic analysis (Figure 9) indicates the presence of at least two components having

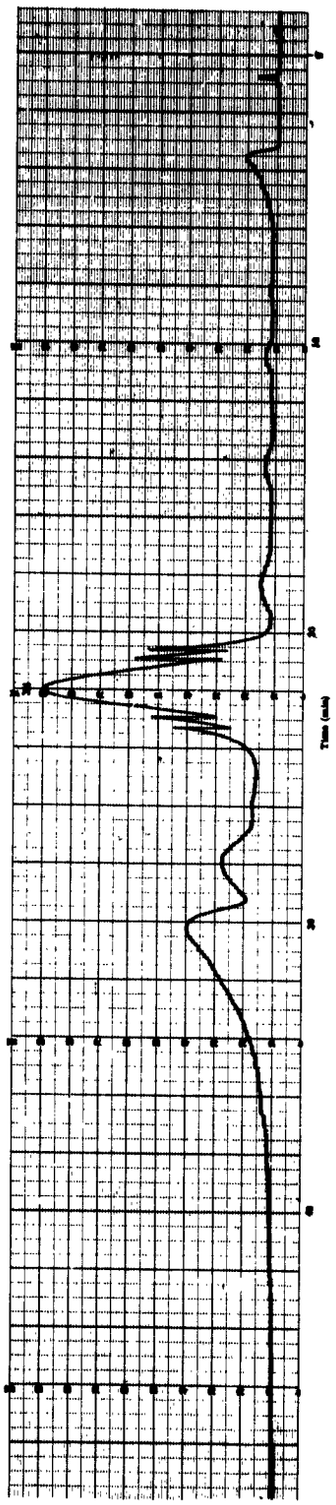


Figure 1. Vapor-Phase Chromatogram of Fluorination Product - Fraction I

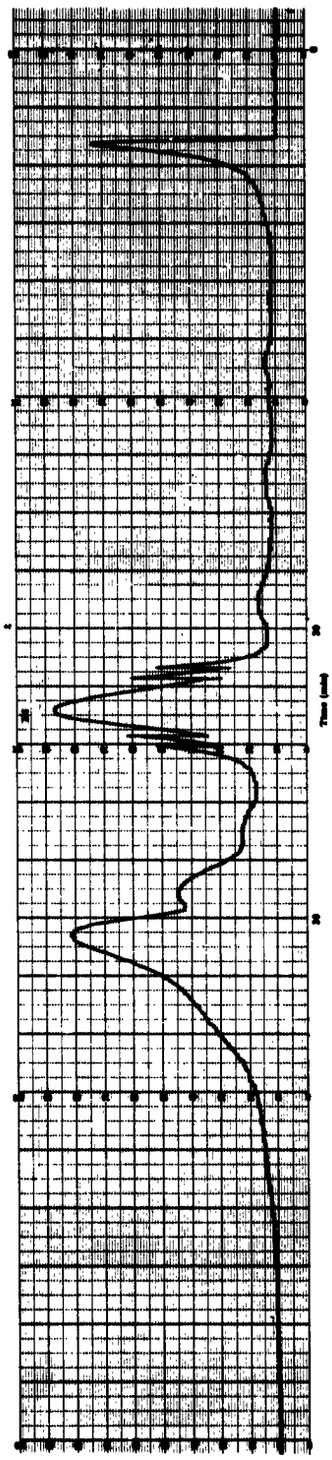


Figure 2. Vapor-Phase Chromatogram of Fluorination Product - Fraction II

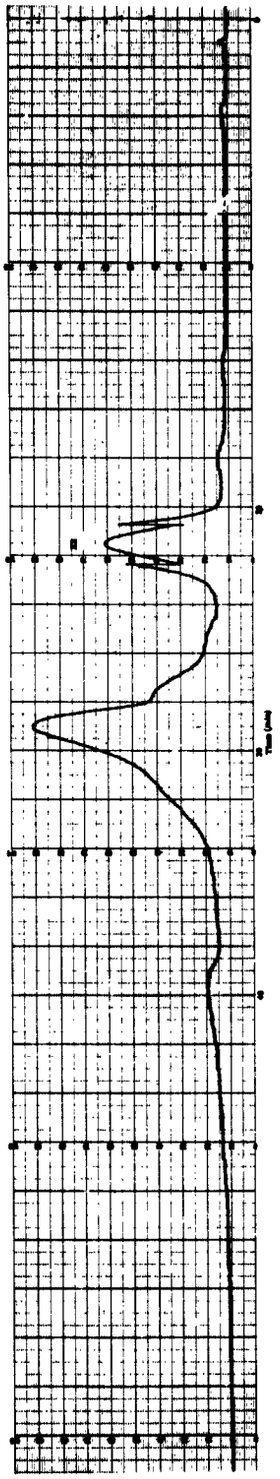


Figure 3. Vapor-Phase Chromatogram of Fluorination Product - Fraction III

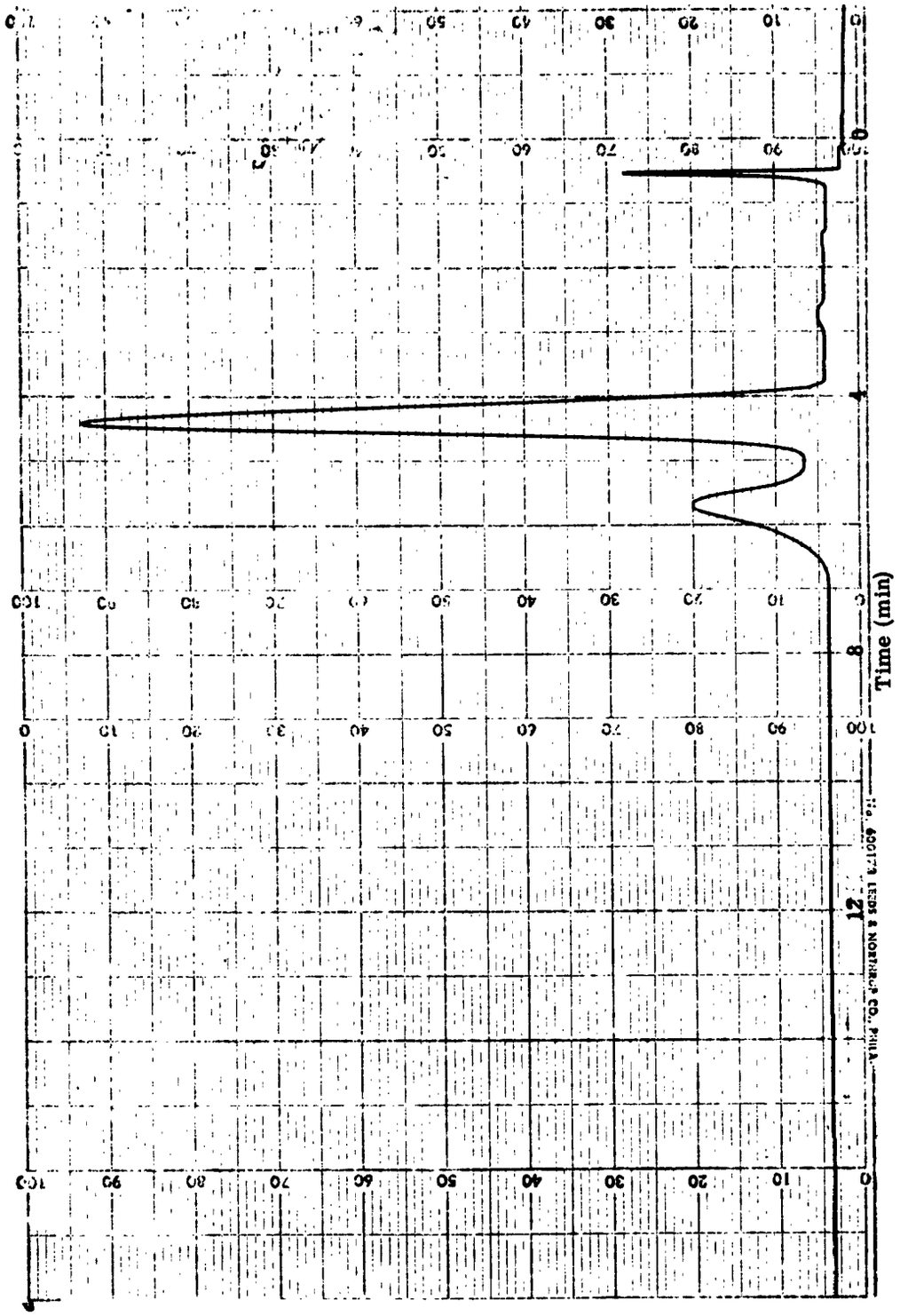


Figure 4. Preparative Scale V.p.c. of Cyclohexy difluoramine - Fraction I

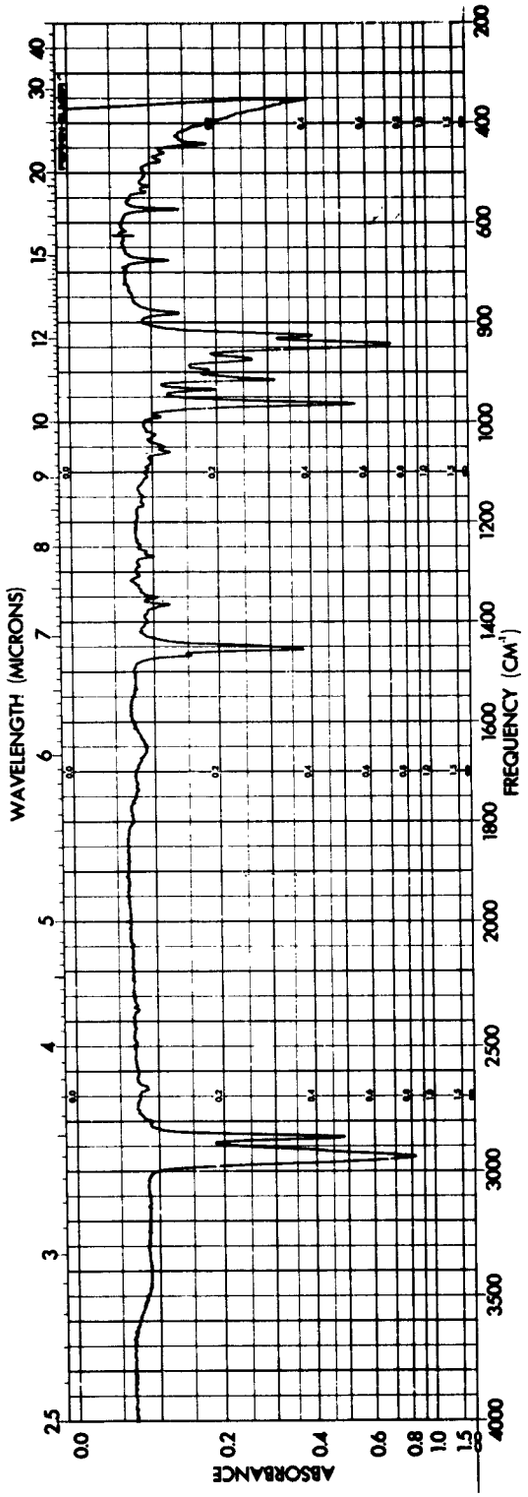


Figure 5. Infrared Absorption Spectrum of Cyclohexyldifluoramine

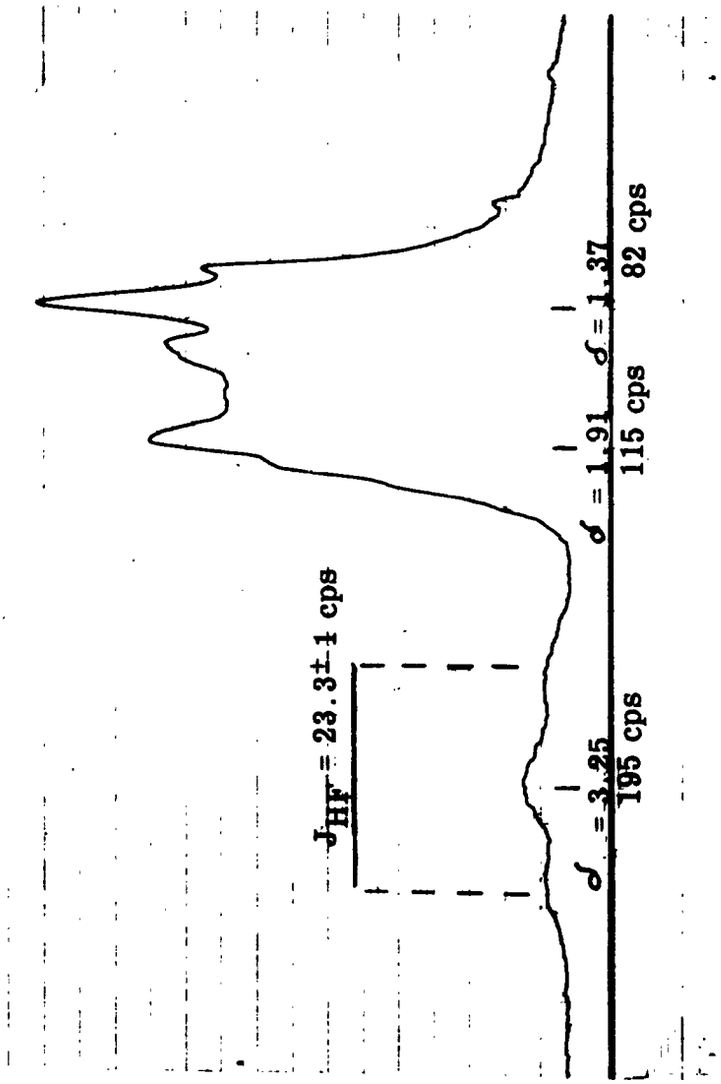


Figure 6. Proton N.m.r. Spectrum of Cyclohexyldifluoramine

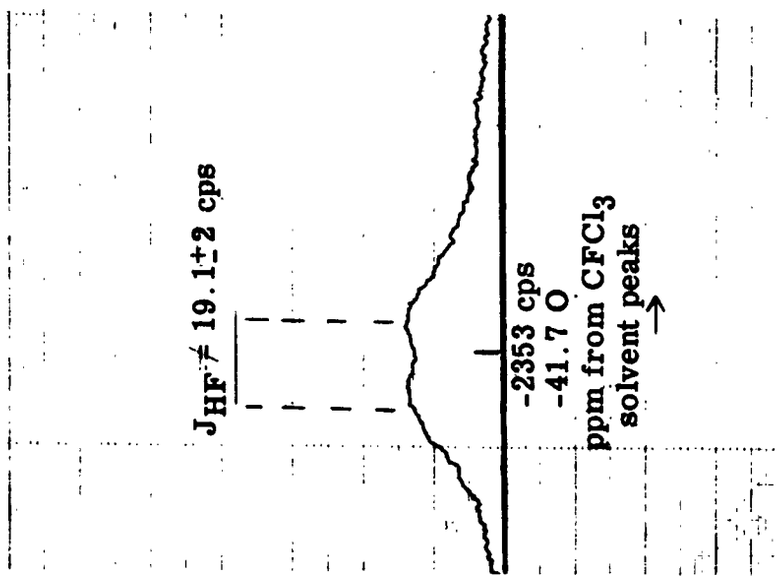


Figure 7. F^{19} N.m.r. Spectrum of Cyclohexyldifluoramine

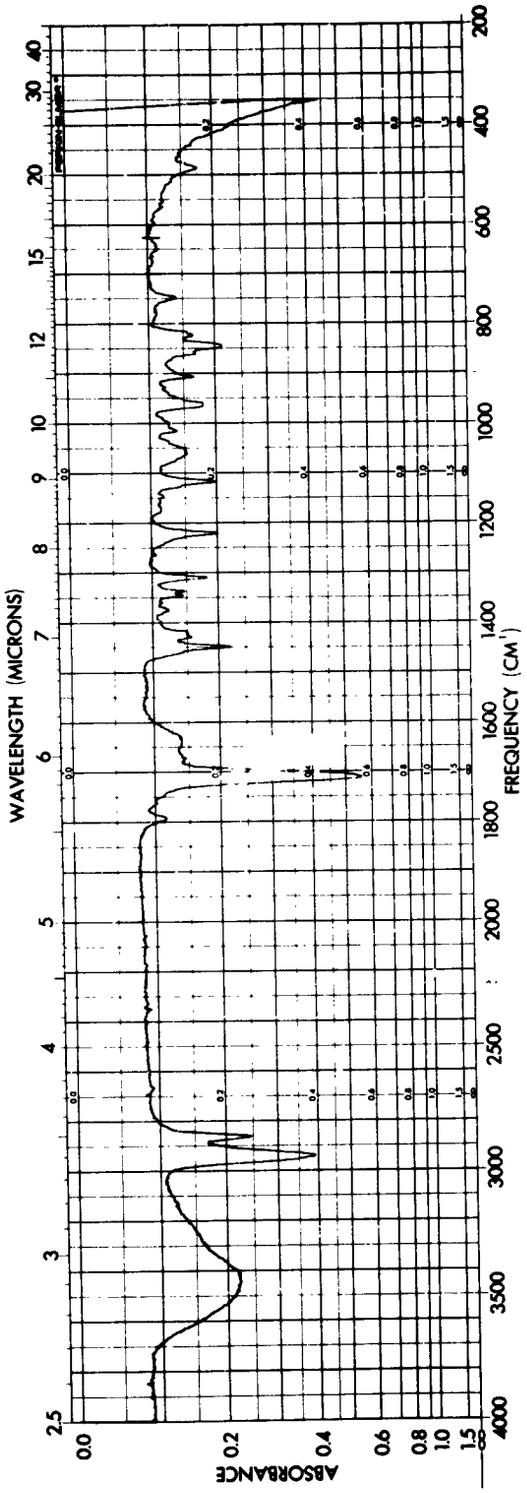


Figure 8. Infrared Spectrum of Ethyl N-Fluoro-N-cyclohexylcarbamate

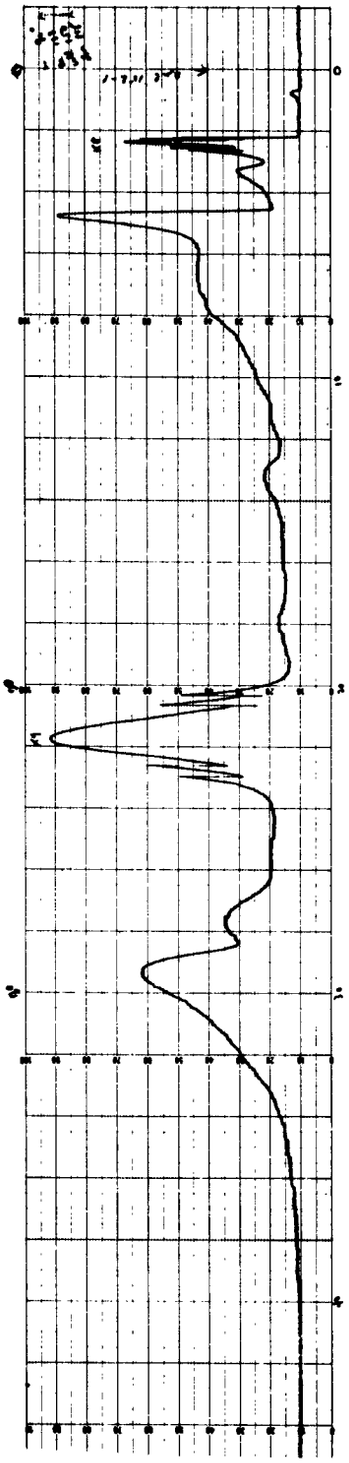


Figure 9. Vapor-Phase Chromatogram of Dehydrofluorination Mixture

shorter retention times than the cyclohexyldifluoramine which constitutes the bulk of the reaction mixture, but the quantities involved are small. The reason for the failure of II to eliminate HF to any significant extent under conditions which have proven effective for other secondary alkyldifluoramines is not yet understood.

3. Reaction of Heptanal with Difluoramine

An N,N,N'-trifluoroalkylamidine was sought for further studies of the chemistry of the >C=NF group. The n-heptyl derivative was chosen (Ref 4) as a suitable model compound because of its low sensitivity and the ready availability and relative stability of the corresponding aldehyde.

The reaction of n-heptanal (V) with difluoramine has been found to give varying yields of 1,1-bis(difluoramino)heptane (VI) and bis(1-difluoramino-heptyl) ether (VII), depending upon the relative concentrations of reactants and the rate of addition of the aldehyde. The results of seven runs are

$$\underset{\text{V}}{C_6H_{13}CHO} + 2HNF_2 \xrightarrow{H_2SO_4} \underset{\text{VI}}{C_6H_{13}CH(NF_2)_2} + \underset{\text{VII}}{(C_6H_{13}CHNF_2)_2O} \qquad (5)$$

summarized in Table I.

The products were isolated by vacuum distillation and characterized by elemental analyses, infrared spectra, proton and F^{19} N.m.r. spectra; and in the case of VI by comparison of physical properties with reported values (Ref 8).

$$RCHO + NHF_2 \longrightarrow R\overset{H}{\underset{NF_2}{C}}-OH \underset{}{\overset{H+}{\rightleftharpoons}} \left[R\overset{H}{\underset{NF_2}{C}}-\overset{+}{OH}\ H\right] \xrightarrow{-H_2O} R\overset{H}{\underset{NF_2}{C}}+ \qquad (6)$$

TABLE I

REACTION OF HEPTANAL WITH DIFLUORAMINE

Expt. No.	HNF_2 mmoles	RCHO mmoles	Conditions	Products: gem-cpd mmoles	gem-cpd %	Ether mmoles X2	Ether %
1	253	50	b	0	0	11	22
2	275	50	c	17.5	35	4	8
3	320	53	d	20	38	5	20
4	320	26	d	12.5	47	0.5	3.6
5	280	53	d	21.3	40	2.4	9
6	280	53	d, e	5.2	10	3.7	12
7	280	53	d, e	5.7	11	5.9	22

Notes:

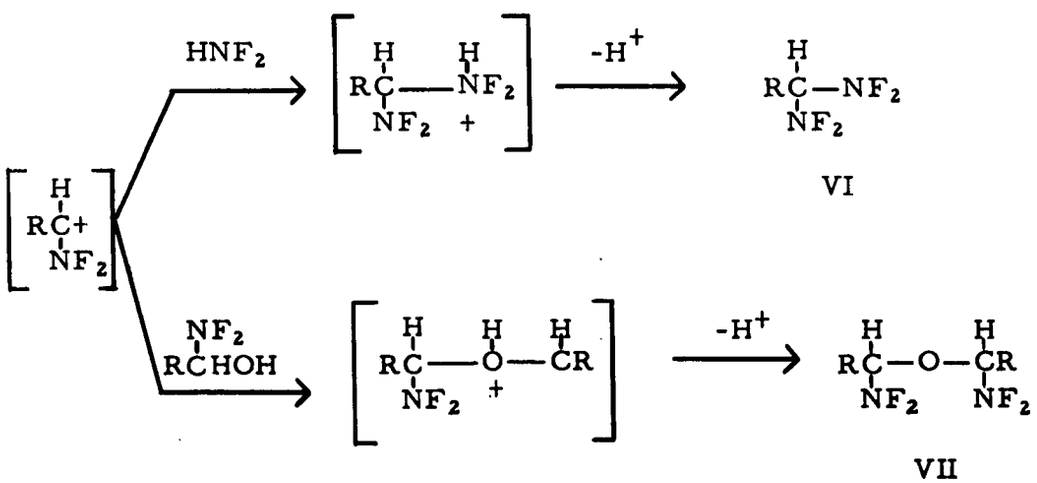
a. All expts done at 0° in 5.0 mL 105 % fuming N_2SO_4

b. RCHO added while HNF_2 was being generated

c. RCHO added during 105 min. after all HNF_2 was present, refluxed 105 min.

d. RCHO added after all HNF_2 was present refluxed 4 hr.

e. Inadvertent use of CCl_4 in the Dry Ice condenser in place of $CHCl_3/CCl_4$ mixture gave the higher reflux temperature. The substantial loss of HNF_2 permitted the formation of the ether at the expense of gem-bis(difluoramine).



(7)

(8)

A large excess of difluoramine and/or the slow introduction of aldehyde would favor the reaction shown in equation 7, producing the desired gem-compound, VI. If the local concentration of aldehyde is permitted to build up, on the other hand, formation of the ether (VII) by equation 8 becomes more probable.

The F^{19} n.m.r. spectrum of VII (Ref 4) consisted of an extraordinary AB quartet with J greater than $\Delta\nu$. The smaller splittings are due to coupling with hydrogen atoms gem to difluoramino groups. The observed resonances indicate that both difluoramino groups are identical, but that the two fluorine atoms in each group differ from each other in their environments. Such a situation requires that rotation about the carbon-nitrogen bonds be restricted, although such restriction is not clearly evident from examination of Fisher-Hirschfelder models. The problem is further complicated by the assymmetry of carbon atoms.

4. Dehydrofluorination of 1,1-Bis(difluoramino)heptane

The weakly basic ion-exchange resin, which has proven to be an effective reagent for the dehydrofluorination of 1,2-bis(difluoramino)cyclohexane and 1,2- and 1,4-bis(difluoramino)cyclohexenes (Ref 9), was applied in the dehydrofluorination of 1,1-bis(difluoramino)heptane (VI). Using the customary two-fold excess of resin, a liquid compound containing nitrogen and fluorine was obtained. The results of elemental analysis revealed, however, that two equivalents of hydrogen fluoride had been removed. The infrared spectrum of the product included, in addition to the expected C-H and N-F absorptions, a

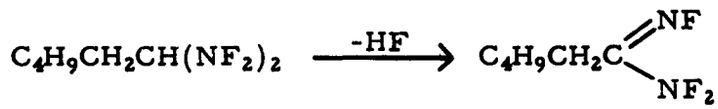
$$\underset{\text{VI}}{C_6H_{13}CH(NF_2)_2} + 2B \not\longrightarrow \underset{\text{VIII}}{C_6H_{13}C\begin{matrix}=NF\\ -NF_2\end{matrix}} + BHF + B \qquad (9)$$

band at 1642 cm^{-1} indicating unsaturation (C=C or C=N) and a strong sharp band at 1550 cm^{-1}, probably due to a ring vibration (Ref 4).

Several plausible structures can be postulated for a compound having these features and the empirical formula $C_7H_{12}N_2F_2$. Mass spectral evidence (Ref 4) effectively eliminated any dimeric structure from consideration, since no mass peaks greater than 162 were observed. The boiling point, 35 - 38° (2.5 mm.) 61 - 63° (20 mm.), was also in accord with this conclusion. The detection of unsaturated fragments in the mass spectrum was contradicted by the proton NMR spectrum, which failed to show any olefinic C-H. The F^{19} n.m.r. spectra

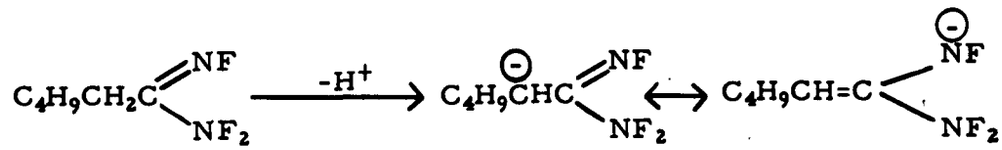
included resonance peaks at -45.9, -42.5, -16.1, and 9.8 p.p.m. from $CFCl_3$, attributable to N-F, and a weak triplet at +138.6 p.p.m., possibly due to C-F.

A careful weighing of all the evidence leads to the suggestion that the product has the fluoriminoazirane structure (IX). One may assume the initial formation of the amidine VIII by normal E_2 elimination, and subsequent removal of the proton which would be expected to be activated by the electronegativity of the difluoramino and fluorimino groups. The carbanion (X) can rearrange by an internal nucleophilic attack (SN 1) on nitrogen; subsequent elimination of fluoride ion would result in the formation of IX.



(10)

VI VIII



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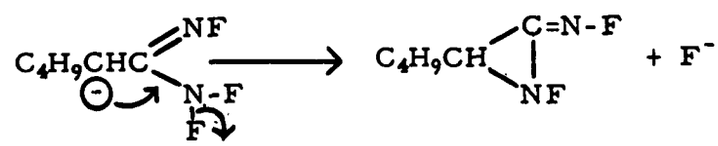
VIII X XI



(12)

XI IX

When the reaction described above was repeated, using a single equivalent of ion exchange resin and maintaining the reaction temperature at 16-20°, a different result was obtained. The liquid product contained N-F groups and unsaturation, but lacked the strong absorption at 1550 cm^{-1}. The presence of water, presumably introduced into the system with the ion exchange resin, made more detailed interpretation of the spectrum impossible.

An attempt to repeat this 1:1 reaction on a larger scale, in order to obtain sufficient material for identification, produced an interesting result. Due to a

mechanical failure, the reaction mixture was heated to 40° for a short period. Under these conditions even though only one equivalent of the base was present, the product obtained was identical to IX. Further work will be required to determine the necessary conditions for the synthesis of the amidine and to characterize the product IX.

B. EXPERIMENTAL

1. Cyclohexyldifluoramine

(a) In a 1-l. flask equipped with a large magnetic stirring bar, 68.5 g. (0.40 mole) of ethyl-N-cyclohexylcarbamate (m.p. 52 - 54.5°) was suspended in 70 ml. of distilled water. The flask was cooled in an ice bath and maintained at 5 - 8° for 3 hr. while 0.88 mole of fluorine, diluted to 20% with nitrogen, was introduced. During the reaction the finely divided solid gradually coagulated to a pasty mass. The reaction mixture was diluted with 75 ml. CH_2Cl_2 and separated. The acqueous layer was extracted twice with 30 ml. CH_2Cl_2 and the extracts were combined with the solvent layer and dried over Na_2SO_4. After the solvent was removed at atmospheric pressure, the residue was distilled to yield three fraction:

(1) 3.0 g. at 28 - 45° (23 mm.)
(2) 1.5 g. at 48 - 63° (23 mm.)
(3) 4.0 g. at 30 - 90° (0.25 mm.)

There remained a residue of 50.1 g. of tan waxy solid which proved to be impure ethyl-N-cyclohexylcarbamate.

(b) In a 1-l. flask equipped with a large magnetic stirring bar, 68.5 g. (0.40 mole) of ethyl-N-cyclohexylcarbamate was suspended in 600 ml. distilled water containing 0.2 g. "Tergitol Non-ionic NP-35." The flask was cooled in an ice bath and maintained at 10 - 14° during 6 hr. while 2.0 moles of fluorine, diluted to 20% with nitrogen, was bubbled through. The reaction mixture was worked up as above. The solvent was collected in a trap cooled with Dry-Ice as it distilled off, and a sample was analyzed by v.p.c. No trace of a second component could be detected. Distillation of the product mixture yielded:

(1) 1.14 g. at 25 - 35° (26-27 mm.)
(2) 1.41 g. at 37 - 41° (26-27 mm.)
(3) 8.13 g. at 41 - 70° (0.10-0.12 mm.)
(4) 32.2 g. solid residue.

Analytical v.p.c. curves were obtained using a 6-ft. by 1/4 in. column, packed with silicone SF-96 on 60/80 firebrick, under the following conditions:

Column Temp:	90°	Detector Temp:	150°
Injector Temp:	115°	Collector Temp:	133°
Sample :	$2\mu l$.	Flowrate :	30 ml./min.
Attenuation :	X 1, except as noted.		

2. Dehydrofluorination of Cyclohexyldifluoramine

Approximately 4.5 g. (33.3 mmoles) of crude cyclohexyldifluoramine (containing some ethyl N-fluoro-N-cyclohexylcarbamate) was dissolved in 250 ml. ethyl ether. Amberlite IR-45 ion-exchange resin (6.6 g., 33.0 meq.) was added in small increments during four hours. The flask was flushed with N_2 and the contents stirred at room temperature for an addition 16 hr. The resin beads disintegrated but did not change color. The suspension was filtered and the filtrate was dried over $CaSO_4$ and Na_2SO_4 and distilled. A pale yellow liquid product was obtained, 0.95 g.

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CONFIDENTIAL

Thiokol
REACTION MOTORS DIVISION

SECTION II

SYNTHESIS OF COMPOUNDS FOR STRUCTURE-SENSITIVITY STUDY

A. P. Kotloby

Report RMD 5043-64-F

RMD Project 5043, Task 52
Report Period: 1 January 1964 to
31 December 1964

Contract No. NOnr 4364(00)
ARPA Order No. 417
Project Code 4910

CONFIDENTIAL

FOREWORD

The research reported in this section of the final report was administered under the direction of the Power Branch, Office of Naval Research, with Mr. R. L. Hanson as Project Engineer.

This section covers work conducted during the period from 1 January 1964 to 31 December 1964 on synthesis of compounds for structure-sensitivity study.

The following personnel participated in this research: A. P. Kotloby (Project Scientist), W. H. Wieting (Synthesis), J. A. Creatura, D. N. Pregler, and D. F. Kates (Instrumental and Wet Chemical Analysis).

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I. INTRODUCTION

This portion of the advanced oxidizer research program represents the synthetic phase of a study aimed at an understanding of the structural and chemical factors affecting the sensitivity of organic difluoramines. One of the principal problems involved in the use of these compounds in propellant formulations is their sensitivity to applied stresses such as heat and mechanical shock. The evaluation of sensitivity data gathered from a sufficiently large number of organodifluoramines, representing a variety of structural types and functional groups, should be useful in guiding research toward the synthesis of compounds having a minimum degree of sensitivity in relation to their energy content.

In accordance with this goal, Thiokol Chemical Corporation, Reaction Motors Division, undertook the task of preparing a variety of organic difluoramines for sensitivity evaluation by the Naval Ordnance Laboratory, White Oak, Silver Spring, Maryland. These compounds were selected to provide the maximum amount of information on the effects of factors such as the NF_2-to-carbon ratio and type of NF_2 substitution on sensitivity. The sensitivity of these compounds is being measured by the thermal explosion delay test (Ref 1) and some of the data obtained on the products from the synthesis effort have been described by Rosen, et al (Ref 2 and 3). These results show some interesting and potentially valuable correlations between structure and sensitivity for the vicinal and geminal bis(difluoramines). This synthesis work has been extended during the current year to include the preparation of tris(difluoramine)methoxy derivatives. Wherever possible, the difluoramino derivatives were purified to at least 99 percent purity by distillation and gas chromatography.

II. DISCUSSION

A. BACKGROUND OF PROBLEM

The selection of specific organic N-F compounds for synthesis has been based primarily on the following considerations:

- The usefulness of the compounds in providing information relating structure to sensitivity
- Synthetic feasibility
- Requirements of the sensitivity test
- The potential utility of the class of compounds in propellants
- Availability of compounds from other sources.

1. Relationship of Structure to Sensitivity

Structural factors which might be expected to affect the sensitivity of a propellant molecule and which could be evaluated without excessive synthetic difficulties included: (a) the type of difluoramino group substitution (e.g. vicinal, geminal, etc.), (b) the overall oxidative balance of the molecule, (c) the nature of the carbon skeleton (branching, rings, etc.), and (d) the presence of functional groups in the molecule.

Previously, homologous series of aliphatic and alicyclic compounds containing vicinal and geminal NF_2 groups were prepared and a limited number of compounds containing ester, ketone, hydroxy, fluoro, and other functional groups were synthesized. It became of interest during the past year of the program to extend the studies to the energetic 1,1,1-tris(difluoramino)methoxyalkanes.

2. Synthetic Feasibility

The syntheses of the NF-compounds employed in this work are based on known reactions of difluoramine, tetrafluorohydrazine, and perfluoroguanidine

with suitable organic compounds. While the applicability of these reagents has certain definite limitations, it is possible by using these methods to prepare a sufficiently wide variety of organodifluoramino structures to eludicate most of the structural factors which might be expected to affect the sensitivity of these materials.

3. Requirements of the Sensitivity Test

The test requirements are quite important in the selection of compounds for evaluation. Strong emphasis is being placed on the use of a high-temperature explosion delay test for evaluation of sensitivity (Ref 1). This test requires a compound which is liquid at room temperature, or a solid that melts without decomposition. Another requirement is that the compound should be sufficiently sensitive to yield meaningful results. Regarding this point, as a rule of thumb, it has been found that a NF_2/C ratio less than 1:3 is generally undesirable.

4. Potential Utility in Propellants

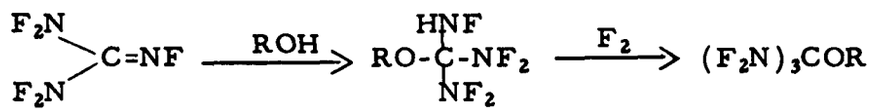
Since the primary purpose of the extensive research currently being conducted in N-F chemistry is the development of more energetic propellant systems, the possibility that a compound or class of compounds will ultimately be used as a propellant has a definite bearing on whether it should be included in this program. This consideration is considerably modified, however, by two other factors, namely: (1) the fact that basic structure-sensitivity data on any N-F compound can be of use in synthetically "designing" new propellant molecules, and (2) that it is not possible to state precisely at this time which compounds, or classes of compounds, are most likely to find ultimate use in propellants. Nevertheless, all else being equal, the most energetic materials will be of greatest propellant interest, and this, in turn, means those compounds with the highest NF_2 content. This accounts for the current interest in the preparation and purification of tris-compounds on this program.

5. Availability of Compounds from Other Sources

The Naval Ordnance Laboratory maintains contact with other research groups in the propellant industry and occasionally receives N-F compounds from them for sensitivity investigations. Close liaison is maintained between Thiokol Chemical Corporation, Reaction Motors Division, and Naval Ordnance Laboratory personnel to avoid any duplication in the synthesis of specific compounds on this program.

B. SYNTHESIS OF TRIS(DIFLUORAMINO)METHOXYALKANES

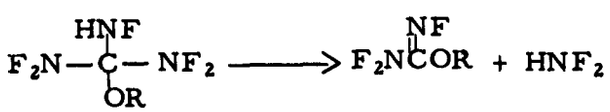
Tris(difluoramino)methoxyalkanes can be prepared by the nucleophilic addition of alcohols to perfluoroguanidine followed by the fluorination of the resulting fluoramino adduct (Ref 4 through 6).



(1)

I

RMD has synthesized and investigated the gas chromatographic purification of a series of tris(difluoramino)methoxyalkanes from primary alcohols containing four to nine carbon atoms, and from a limited number of secondary alcohols (Ref 7), using the sequence of reactions shown in equation (1). The initially formed fluoramino adducts (I), obtained in 80 to 90 percent yield, could be distilled without decomposition under reduced pressure, but had only limited stability when stored at 0 to 5°C in a glass container. The infrared spectra of freshly prepared material showed, in addition to NF absorptions (10.3, 11.1, 11.6μ), strong absorptions at 3.04μ corresponding to the N-H deformation. A partially decomposed sample showed the presence of the >C=N bond at 5.96 to 6.10μ [King (Ref 14) gives 6.11 to 6.31μ for the position of the >C=N absorption of N,N-dialkyl-N'-p-toluenesulfonyl amidines] indicating that some elimination of difluoramine had taken place:



(2)

II

The bis(difluoramino)fluoraminomethoxy derivatives (I) were then fluorinated at 0°C with two to 10 percent fluorine diluted with nitrogen. Acetonitrile is the preferred solvent for the reaction because when it is used there is less fluorination of the alkyl chain. The use of sodium fluoride as an HF scavanger in the fluorination step was found to cause an exothermic reaction accompanied by gas evolution, giving a nearly quantitative yield of colorless liquid, which was identified as the fluorimino derivative (II). The structure of

$$F_2N\text{-}C(HNF)(NF_2)\text{-}OR \xrightarrow[CH_3CN]{NaF,\ 25^\circ} F_2NC(NF)OR + [HNF_2] \qquad (3)$$

II

the product was established by its infrared and nuclear magnetic resonance spectra. In the case of difluoraminofluoriminomethoxyheptane, we observed that the product consisted of a 3:2 mixture of syn- and anti-isomers. The NMR data showed the following composition:

syn: -37.3 ϕ (NF_2) + 51.4 ϕ (C=NF)

anti: -42.6 ϕ (NF_2) + 43.4 ϕ (C=NF)

Elimination of sodium fluoride from the reaction did not completely prevent the formation of the fluorimino derivative, but it reduced the amount of (II) formed as a byproduct.

Based on the NMR measurements, the crude reaction products from the fluorination of equation (1) assayed 80 to 90 percent tris(difluoramino)methoxyalkane. Impurities containing the following functional groups were identified by the infrared and NMR measurements:

$>C(F)H$, $>C{=}NF$, $-C(F)_x-$

The probable structures of these impurities are shown below:

$RO\text{-}C(HNF)(NF_2)\text{-}N_2F$, $RO\text{-}C(NF)\text{-}NF_2$, $RO\text{-}C(F)(NF_2)\text{-}NF_2$, $R_fOC(NF_2)_3$

(where R_f = partially fluorinated alkyl chain).

In Table I are listed experimental conditions and results obtained in the synthesis of the intermediate fluoramino adducts. Data on the preparation of the fluorinated products are given in Table II. The uptake of perfluoroguanidine in the first reaction was nearly quantitative. Infrared analysis of the residual gas at the end of the reaction showed it to be unreacted perfluoroguanidine contaminated with traces of the solvent. The amount of the unreacted perfluoroguanidine corresponded approximately to the excess over the theoretical quantity

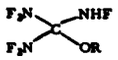
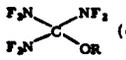
TABLE I

CONDITIONS USED IN SYNTHESIS OF BIS(DIFLUORAMINO)FLUORAMINOMETHOXYALKANES

Alcohol	Moles	PFG (moles)	Freon-113 (ml)	Urea (gm)	Time (hr)	Temp (°C)	Yield (crude) (%)	Remarks
Butanol	0.03	0.05	10	1.0	16	0→23	---	Not isolated; fluorinated directly
Butanol	0.03	0.05	20	0.3	16	0→25	~90	Very shock sensitive; IR shows strong NH absorptions at 3300 cm^{-1}
Pentanol	0.05	2x0.015	10	---	32	20	0	Starting material recovered
Pentanol	0.045	0.05	10	1.0	16	24	---	Not isolated; fluorinated directly
Pentanol	0.03	0.05	20	0.3	16	0→32	83	Shock sensitive; NH absorption at 3300 cm^{-1}
Pentanol	0.03	0.05	20	0.3	16	0→36	92	Shock sensitive; NH absorption at 3300 cm^{-1}
Pentanol	0.03	0.05	20	0.3	16	0→36	92	Shock sensitive; NH absorption at 3300 cm^{-1}
2-Pentanol	0.03	0.05	10	0.3	16	0→25	90	Shock sensitive; NH absorption at 3300 cm^{-1}
3-Pentanol	0.03	0.05	20	0.3	16	0→23	---	Not isolated; fluorinated directly
Hexanol	0.03	0.05	20	1.0	16	0→27	89	Not isolated; fluorinated directly
Hexanol	0.03	0.05	20	0.3	---	---	---	Glass reactor broke
Hexanol	0.03	0.05	10	0.3	16	0→28	82	Shock sensitive; strong NH absorption at 3300 cm^{-1}
Hexanol	0.03	0.05	20	0.3	16	0→31	82	Shock sensitive; strong NH absorption at 3300 cm^{-1}
2-Hexanol	0.03	0.05	10	1.0	16	0→21	---	Not isolated; fluorinated directly
2-Hexanol	0.03	0.05	10	0.3	---	---	---	Explosion during condensation of PFG
3-Hexanol	0.03	0.05	10	0.3	16	0→19	---	Shock sensitive; strong NH absorption at 3300 cm^{-1}
1-Heptanol	0.03	0.05	10	1.0	16	0→26	---	Borderline sensitivity; strong NH absorption at 3300 cm^{-1}
1-Heptanol	0.03	0.05	20	0.3	32	0→29	99	Borderline sensitivity; strong NH absorption at 3300 cm^{-1}
1-Heptanol	0.03	0.05	20	0.3	16	0→28	---	Borderline sensitivity; strong NH absorption at 3300 cm^{-1}
1-Octanol	0.03	0.05	10	1.0	16	0→28	100	No fire under hammer; NH absorption at 3300 cm^{-1}
1-Octanol	0.03	0.06	20	1.0	16	0→23	90	No fire under hammer; NH absorption at 3300 cm^{-1}
1-Octanol	0.03	0.05	20	1.0	16	0→22	86	No fire under hammer; NH absorption at 3300 cm^{-1}
1-Nonanol	0.04	0.06	---	1.0	---	25	---	Acetonitrile (10 ml) used instead of Freon-113; explosion soon after reaction started
1-Nonanol	0.04	0.06	10	1.0	16	0→29	---	No fire under hammer; NH absorption at 3300 cm^{-1}
1-Nonanol	0.03	0.05	10	1.0	16	0→30	95	No fire under hammer; NH absorption at 3300 cm^{-1}

TABLE II

CONDITIONS USED IN SYNTHESIS OF TRIS(DIFLUORAMINO)METHOXYALKANES

 where R =	BP (°C/mm Hg)	Freon-113 (ml)	Acetonitrile (ml)	NaF (gm)	 (crude) Yield (%)	BP (°C/mm Hg)	Remarks
$-(CH_2)_2CH_3$	---	10	---	---	---	51-52/10.3	Very shock sensitive; IR shows absorptions due to NH, NF and possibly CF
$-(CH_2)_3CH_3$	52-53/4.2	---	20	---	68	44-48/6.0	Analysis pending; F_2:adduct (mole ratio is 2)
$-(CH_2)_4CH_3$	---	10	---	---	---	---	Shock sensitive; g.c. shows two major components identified by IR as a mixture of C-NH and C-NF_2 derivatives
$-(CH_2)_4CH_3$	46/1.0	---	20	2	69	40/6.5	Shock sensitive; g.c. shows two major components identified by IR as C=NF (1640-1680 cm^{-1}) NH (3300 cm^{-1})
$-(CH_2)_4CH_3$	38-40/1.4	---	20	2	40	---	Shock sensitive; g.c. shows two major components identified by IR as C=NF (1640-1680 cm^{-1}) NH (3300 cm^{-1})
$-(CH_2)_4CH_3$	59-63/5.6	---	20	---	95	52-56/4.2	Shock sensitive; g.c. shows two major components identified by IR as C=NF (1640-1680 cm^{-1}) NH (3300 cm^{-1})
$-CH(CH_3)(CH_2)_2CH_3$	---	10	---	---	---	---	Shock sensitive; IR shows strong absorptions at 1640-1680 cm^{-1}
$-CH(CH_2CH_3)_2$	---	20	---	---	---	---	---
$-(CH_2)_5CH_3$	---	20	---	---	89	41-43/0.3	Shock sensitive; IR shows strong absorptions at 1640-1680 cm^{-1} (C=NF)
$-(CH_2)_5CH_3$	48-50/1.6	---	20	2	30	44-47/4.1	
$-(CH_2)_5CH_3$	46-50/1.6	---	20	2	72	44-47/4.1	
$-CH(CH_3)(CH_2)_3CH_3$	---	10	---	---	99	34/0.4	---
$-CH(CH_2CH_3)(CH_2)_2CH_3$	---	10	---	---	98	42-46/6.7	---
$-(CH_2)_6CH_3$	---	10	---	---	92	48-52/0.3	Borderline sensitivity; strong (IR) absorption in the N-H region and trace of C=N
$-(CH_2)_6CH_3$	58-60/0.4	---	20	2	70	42/0.5	Borderline sensitivity; strong (IR) absorption in the C=N region, no NH
$-(CH_2)_6CH_3$	50-52/0.2	---	20	2	68	42/0.5	Borderline sensitivity; strong (IR) absorption in the C=N region, no NH
$-(CH_2)_7CH_3$	---	10	---	---	92	58-66/0.5	No fire under hammer; IR shows small absorption due to N-H, C=N, and N-F
$-(CH_2)_7CH_3$	62-66/0.5	---	20	2	36	58/0.25	No fire under hammer; IR shows small absorption due to N-H, C=N, and N-F
$-(CH_2)_7CH_3$	55-58/0.7	---	20	2	85	61-62/0.4	No fire under hammer
$-(CH_2)_8CH_3$	77-79/0.45	---	20	2	---	68-70/0.25	No fire under hammer; IR absorptions corresponding to C=N and C-F vibrations
$-(CH_2)_8CH_3$	---	10	---	---	100	70-78/0.7	No fire under hammer; IR absorptions corresponding to N-H and C-F vibrations

Note: F_2:adduct (mole ratio) is 1 in all cases except as noted in Remarks

required by the stoichiometry of the reaction. The addition of urea is known to facilitate this reaction (e.g., Ref 4), and, although no optimum concentrations have been determined, the addition of 0.3 gm of urea per $\sim$0.03 mole of alcohol proved to be sufficient. In cases where no urea was added, the starting materials were recovered unchanged after 32 hours.

Initial efforts to obtain very pure samples of tris(difluoramino) compounds were frustrated by difficulties encountered in the gas chromatographic purification. The reasons for these difficulties are the presence of a considerable number of contaminants in the crude product and the instability of the tris-compounds on the chromatographic columns that were used. In order to better define the gas chromatographic parameters needed to effect purification of the tris-compounds, extensive studies were made on a single compound, tris-(difluoramino)methoxypentane. The types of columns and experimental conditions employed are listed in Table III. In every case where some separation of the reaction mixture was indicated, a change to a larger, preparative scale column (12 to 20 feet by 3/8 inch) resulted in poorer separation and the loss of much of the sample on the column. Attempts to decrease the retention period by increasing the column temperature to 115°C led to the decomposition of the sample. This work indicates that the purification of tris(difluoramino)methoxyalkanes by gas chromatography is extremely difficult, owing to the tendency of the compounds to decompose, even on inert columns at low temperatures (75°C). We believe that it would be advisable, however, to try a nickel or Monel column packed with Kel-F acid on Teflon before investigating other purification techniques (e.g., adsorption chromatography) for the tris(difluoroamino) compounds.

It should be pointed out that difficulties in effecting purification of tris-compounds have also been reported by other laboratories. For example, work at DuPont (Ref 8) has revealed the presence in perfluoroguanidine-derived intermediates of carbonate-type byproducts which may be due to oxidation of the hydroxyl groups during the fluorination. Attempts to remove the C=NF fraction by washing with dilute caustic were unsuccessful. In the same report (Ref 8) it was indicated that tris-NF_2 derivatives could not be obtained in >90 percent purity by adsorption chromatography and/or distillation. Esso (Ref 9) also has experienced considerable difficulty in purifying the same fluorinated pentanol-perfluoroguanidine adduct with which most of our gas chromatographic work has been performed.

The question of purity is obviously extremely important in studying the sensitivity of NF materials. Therefore, further investigation is needed to

TABLE III

CONDITIONS INVESTIGATED IN GAS CHROMATOGRAPHIC PURIFICATION OF TRIS(DIFLUORAMINO)METHOXYPENTANE

Column (Cu tubing passivated with F_2)	Column Temp (°C)	Remarks
6 ft x 3/8 in.; 20% SF-96 a-w Chromosorb P	130	Two major unresolved peaks
6 ft x 3/8 in.; 20% SF-96 a-w Chromosorb P	75	Poor resolution; some decomposition
3 ft x 1/4 in.; 20% SF-96 a-w Chromosorb P	75	Poor-to-good resolution but only with < 5μl injection
6 ft x 1/4 in.; 20% Kel-F Oil a-w Chromosorb P	75	Very broad, unresolved peaks
6 ft x 1/4 in.; 20% Halocarbon Oil 14-25 a-w Chromosorb P	80	Fair separation of 3-5 peaks Resolution needs to be improved
6 ft x 1/4 in.; 20% SF-96 a-w Chromosorb W	80	No resolution
6 ft x 1/4 in.; 20% SF-96 HMDS Chromosorb P	80	Broad peaks, indication of decomposition on column
6 ft x 1/4 in.; 20% Halocarbon Oil 14-25; Fluoropak 80	60-90	Fair but not always reproducible resolution; occasional indication of decomposition of column
Al tubing 20 ft x 3/8 in.	130	Decomposition; no separation

obtain a more complete understanding of the factors controlling the preparation and purification of tris-compounds. The goal of this work will be to make available compounds of > 99 percent purity for evaluation of sensitivity and to ascertain to what extent impurities may be affecting the sensitivity of crude tris-compounds.

C. SYNTHESIS OF BIS(DIFLUORAMINO)ALKANES

The addition of tetrafluorohydrazine to olefins is a general method for preparing vicinal bis(difluoramines). In the case of unhindered olefins containing isolated double bonds, the reaction can usually be carried out at, or slightly below, atmospheric pressure in a glass bulb. For volatile or somewhat less reactive(hindered)olefins, the reaction is best carried out in an all-glass pressure reactor of the Fischer-Porter type (Ref 10), or in a stainless-steel Hoke bomb, at 70 to 100°C under a pressure of 150 to 300 psig. In order to form tetrakis-NF_2 adducts from conjugated dienes, the reaction is carried in two steps. First, at relatively low temperature (60 to 70°C), followed by higher temperatures and pressures (100 to 110°C; 300 to 400 psig; Ref 11). In a typical reaction, a solution of olefin in a solvent (e.g., Freon-113) is charged into the pressure reactor and degassed at -80°C. The solvent moderates the reaction and also desensitizes the reaction products. A measured volume of tetrafluorohydrazine is then condensed into the reactor at -196°C and the contents are heated for a period of three to 24 hours. The amount of crude product is usually in the range of 60 to 80 percent of the theoretical yield. The gem-bis(difluoramines) were prepared by the reaction of HNF_2 with the corresponding aldehyde or ketone in fuming sulfuric acid, as described in References 12 and 16 and in previous reports on this program (Ref 15). Difluoramine was first generated from difluorourea (Ref 17). Tables IV and V list the vicinal and geminal NF_2-adducts prepared during the past year together with some of their physical constants.

Both gem- and vic-bis(difluoramino)alkanes, after distillation under reduced pressure through a short glass column, were purified by gas chromatographic method (Wilkens Autoprep, Model A-700). The usual g.c. parameters were as follows: Cu column, 12 foot by 3/8 inch previously passivated with fluorine; 20 percent Halocarbon Oil 14-25 on Fluoropak-80; column temperature, 70°C; helium flow, 100 ml/minutes. Under these conditions, both gem- and vic-bis(difluoramino)alkanes could be purified without much decomposition on the column. However, in the case of bis(difluoramino)alkyl esters, a significant decrease in the thermal stability was observed when the α-carbon to the carbonyl group bore an NF_2-group. For example, ethyl 2,3-bis(difluoramino)propionate underwent partial decomposition on an inert column at

TABLE IV

PROPERTIES OF VICINAL BIS(DIFLUORAMINES)

Compound	BP (°C/mm Hg)		n_D^{25}
Methyl 3,4-bis(difluoramine)butyrate	46.0/1.5	176.0/760	1.3870
Ethyl 2,3-bis(difluoramino)propionate	60.0/20	152.0/760	1.3745
1,2-Bis(difluoramino)heptane	50.0/7.0	167.0/760	---
1,2-Bis(difluoramino)-4-hydroxypentane	38.0/0.3	---	---
4,5-Bis(difluoramino)pentanol	60.0/0.22	---	---
1,2-Bis(difluoramino)cyclohexane (cis- and trans-mixture)	41.0/5.0	172.0/760	1.4123

TABLE V

PROPERTIES OF GEMINAL BIS(DIFLUORAMINES)

Compound	BP (°C/mm Hg)		n_D^{25}
1,1-Bis(difluoramino)propane	31.0/160	---	---
1,1-Bis(difluoramino)heptane	40.0/5	162.0/760	1.3820
2,2-Bis(difluoramino)heptane	58.0/8.8	162.0/760	1.3873
1,1-Bis(difluoramino)cyclohexane	46.0/10	164.0/760	1.4080
1,1-Bis(difluoramino)-2-methylpropane	35.0/72	---	---

temperatures as low as 70°C, whereas methyl 3,4-bis(difluoramino)butyrate remained stable in the range of temperatures up to 110°C. The nature of the decomposition products is presently being examined. Since decomposition by reversal of the original N_2F_4 addition gives the conjugated system, O=C-C=C, a possible product is ethyl acrylate (equation 4). Another possibility, of course,

$$CH_3CH_2OC(=O)CH(NF_2)-CH_2(NF_2) \xrightarrow[70^\circ C]{\text{g.c. column}} CH_3CH_2OC(=O)CH=CH_2 + N_2F_4 \qquad (4)$$

is a partial or complete dehydrofluorination of the adduct (Ref 14). The α-$CHNF_2$ grouping would be particularly subject to this type of attack.

Samples of chromatographically-pure compounds (five to 15 gm) were submitted to the Naval Ordnance Laboratory for sensitivity evaluation.

III. EXPERIMENTAL

A. N,N-DIFLUOROUREA BY AQUEOUS FLUORINATION

The difluoramine required for this work was generated by the known procedure (Ref 17). A 100-ml, three-neck flask was filled with a solution of 50 gm (0.93 mole) of urea in 600 ml of water. The solution was cooled to 0°C by means of an external ice-water bath. A 20 percent (by volume) mixture of fluorine in nitrogen was bubbled through the vigorously stirred solution, the temperature of which was kept at 0 to 5°C. Over a period of six hours, 2.0 moles of fluorine were bubbled through the solution. The solution was then stirred for an additional hour under a stream of nitrogen. The total volume of solution at the end of the reaction was 670 ml. The titration of the solution (iodometric method) showed on the average the presence of ~four meq/ml of difluoramine. The yield of N,N-difluorourea varied from 70 to 80 percent. In order to avoid the detrimental effect of glass on aqueous N,N-difluorourea (Ref 12), the solution was stored in polyethylene containers.

B. 1,1-BIS(DIFLUORAMINO)HEPTANE

The method of synthesis of geminally substituted difluoramines was based on the original work carried out at Aerojet General Corporation (Ref 16). Heptaldehyde (3.4 gm, 0.03 mole), b_{10} 40 to 42°C was dissolved in 10 ml of methylene chloride and gradually added to a stirred mixture of 101.6 percent-H_2SO_4 (20 ml) and difluoramine (~4 gm, 0.08 mole) kept under reflux at -80°C. The difluoramine was generated by hydrolysis of a 70 percent aqueous solution of N,N-difluorourea with 40 ml of conc. H_2SO_4. After the addition of HNF_2 was completed, the reactants were stirred for three more hours. At the end of this period, the -80°C condenser was brought to room temperature either by the evaporation of the Dry Ice or by flushing with solution of dichloromethane. The reaction mixture was extracted with methylene chloride. The organic layer was washed with aqueous $NaHCO_3$, then with distilled water until it was neutral, and dried over anhydrous $MgSO_4$. The filtered solution was freed of solvent by

evaporation under reduced pressure, and the residue distilled from Aroclor 1242* (b_{760} 325 to 366°C) solution under reduced pressure. The 1,1-bis(difluoramino)heptane was obtained in 83 percent yield (average of four runs) and after gas chromatographic purification on a 12 foot by 3/8 inch fluorine-passivated Cu column, using 20 percent Halocarbon Oil 14-25 on Fluoropak-80 and a column temperature of 70°C, gave the following constants: b_5 40.0°C, b_{760} 162.0°C, n_D^{25} 1.3820. The infrared spectrum and the chromatogram are shown in Figures 1 and 2, respectively.

Anal. Calcd. for $C_7F_4H_{14}N_2$: C, 41.58; H, 6.98; N, 13.85
Found : C, 41.62±0.11; H, 6.92±0.02; N, 13.94

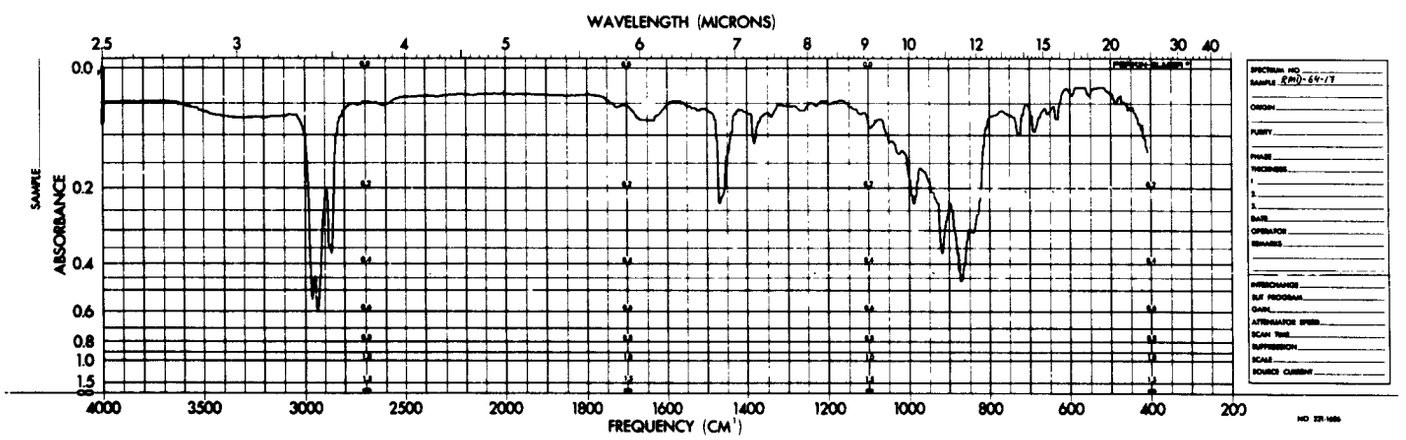


Figure 1. Infrared Spectrum of 1,1-Bis(difluoramino)heptane

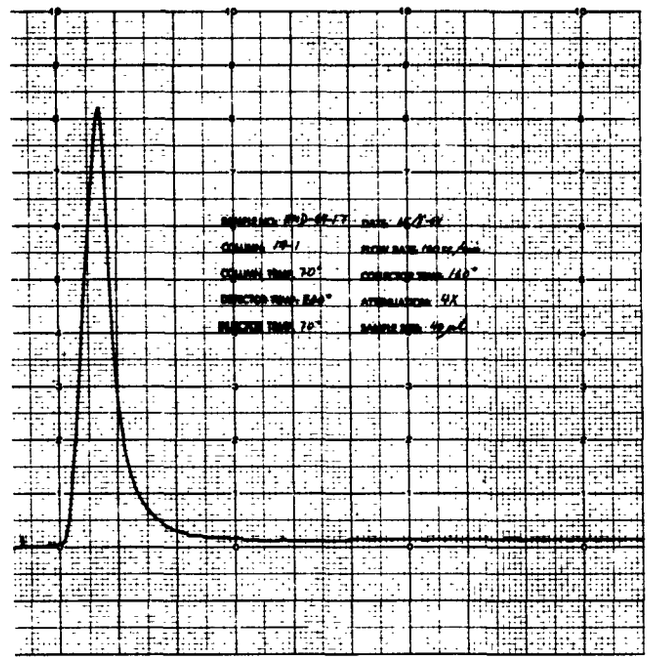


Figure 2. Gas Chromatogram of 1, 1-Bis(difluoramino)heptane

C. 2, 2-BIS(DIFLUORAMINO)HEPTANE

2-Heptanone, b_{760} 149 to 150°C, was treated with difluoramine as described in paragraph B above. The average yield obtained in four runs was 89 percent. Chromatographically pure 2, 2-bis(difluoramino)heptane had the following constants: $b_{8.8}$ 58.0°C, b_{760} 162.0°C, n_D^{25} 1.3873. The infrared spectrum and the chromatogram are shown in Figures 3 and 4, respectively.

Anal. Calcd. for $C_7F_4H_{14}N_2$: C, 41.58; H, 6.98; N, 13.85
Found : C, 41.56 ± 0.15; H, 7.03 ± 0.05; N, 14.01

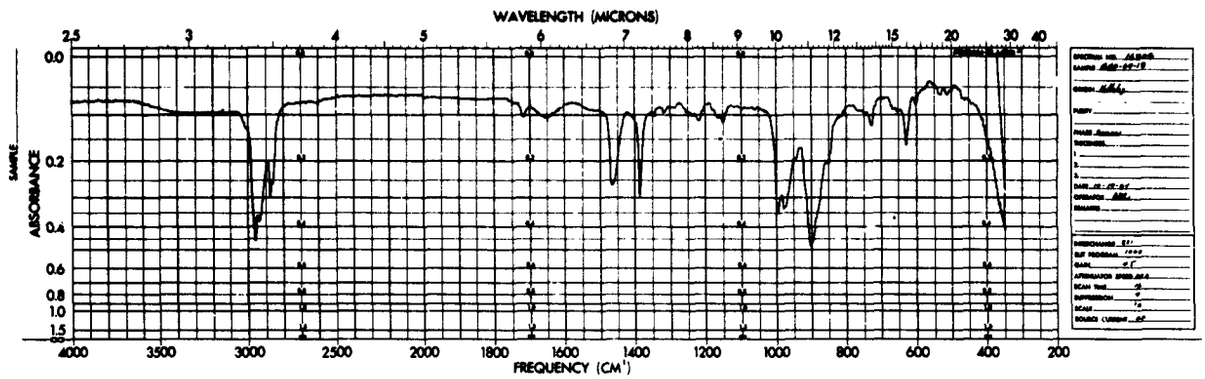


Figure 3. Infrared Spectrum of 2, 2-Bis(difluoramino)heptane

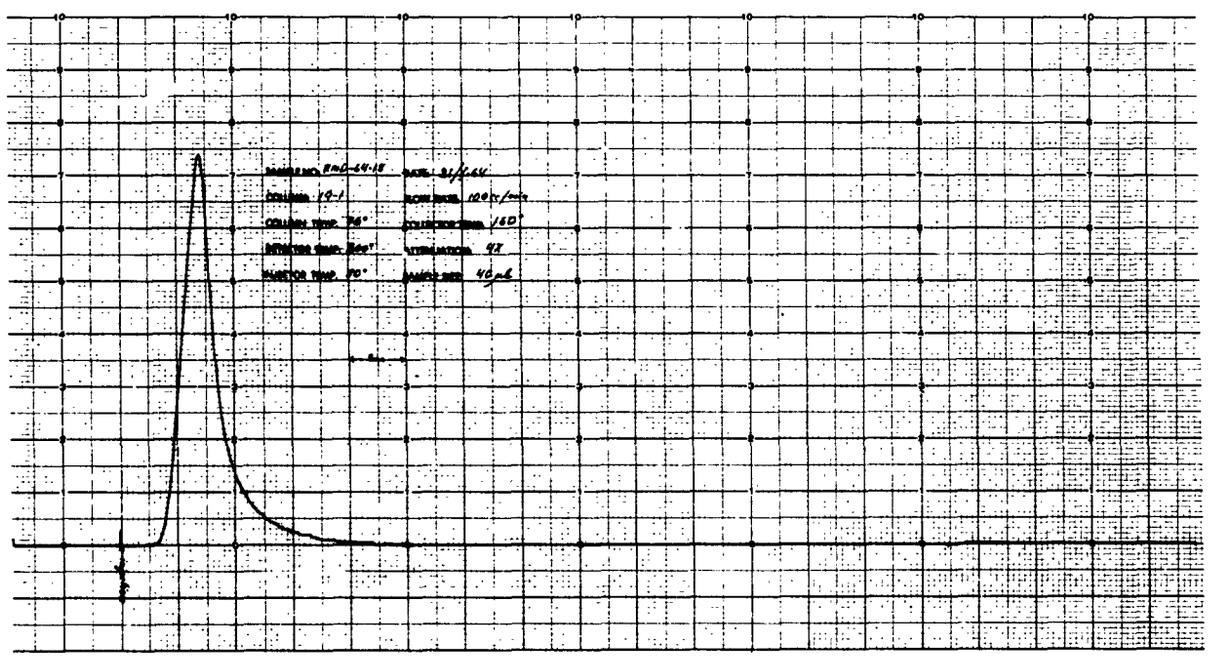


Figure 4. Gas Chromatogram of 2, 2-Bis(difluoramino)heptane

D. 1,2-BIS(DIFLUORAMINO)HEPTANE

Heptene-1 (4.9 gm, 0.05 mole), dissolved in 15 ml of Freon-113, and N_2F_4 (1500 ml, 0.07 mole) were heated overnight at 80°C under an initial pressure of 290 psig in a stainless-steel Hoke cylinder. After stripping off the solvent, 1,2-bis(difluoramino)heptane (81 percent yield, average of five runs) was distilled under reduced pressure. The product was purified by vpc on a fluorine-passivated Cu column, 12 foot by 3/8 inch, using 20 percent Halocarbon Oil 14-25 on Fluoropak-80 and a column temperature of 70°C. The purified product gave the following constants: b_7 50.0°C, b_{760} 167.0°C, n_D^{25} 1.3848. The infrared spectrum and the chromatogram are shown in Figures 5 and 6, respectively.

Anal. Calcd. for $C_7F_4H_{14}N_2$: C, 41.58; H, 6.98; N, 13.85
Found : C, 41.57; H, 7.05; N, 13.94

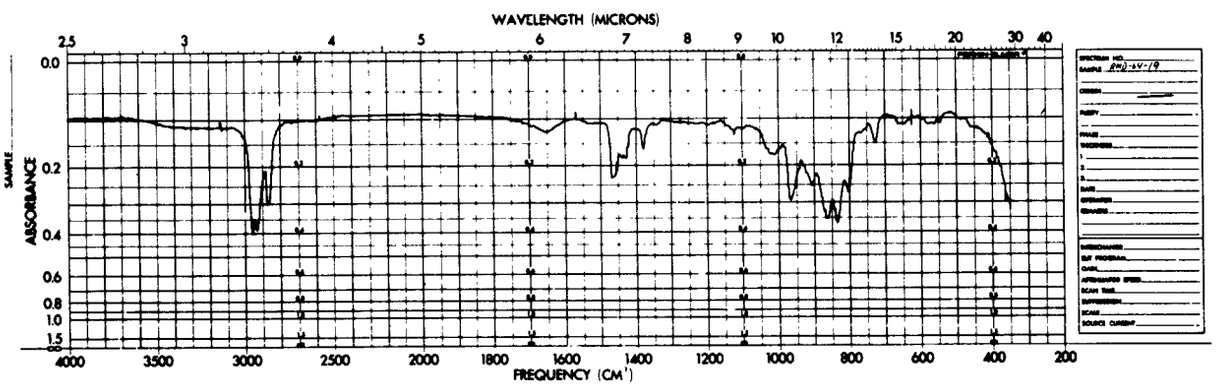


Figure 5. Infrared Spectrum of 1,2-Bis(difluoramino)heptane

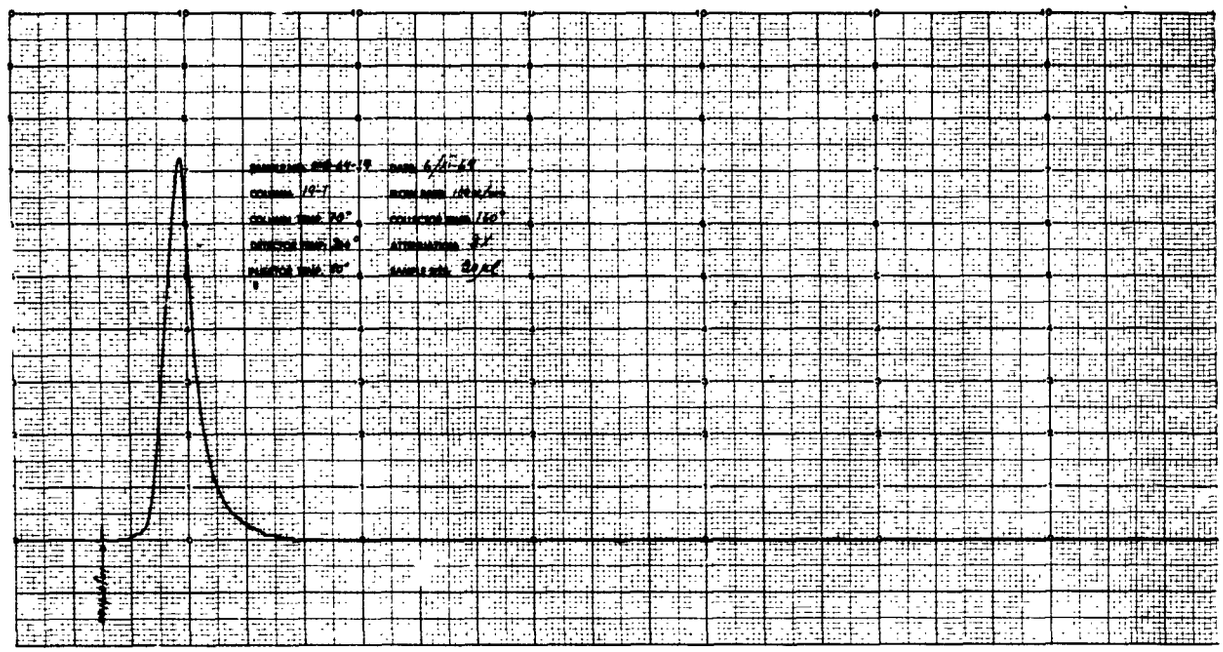


Figure 6. Gas Chromatogram of 1,2-Bis(difluoramino)heptane

E. 1,2-BIS(DIFLUORAMINO)CYCLOHEXANE

Cyclohexene (4.1 gm, 0.05 mole), b_{760} 82.5 to 83.5°C, and N_2F_4 (2000 ml, 0.09 mole) were heated at 90°C overnight in a pressure reactor to give a mixture of cis- and trans-1,2-bis(difluoramino)cyclohexane (92 percent yield, average of 10 runs). After gas chromatographic purification the product gave the following constants: b_5 41.0°C, b_{760} 172.0°C, n_D^{25} 1.4123. The infrared spectrum and the chromatogram are shown in Figures 7 and 8, respectively.

Anal. Calcd. for $C_6F_4H_{10}N_2$: C, 38.71; H, 5.41; N, 15.05
Found : C, 38.68; H, 5.32; N, 14.97

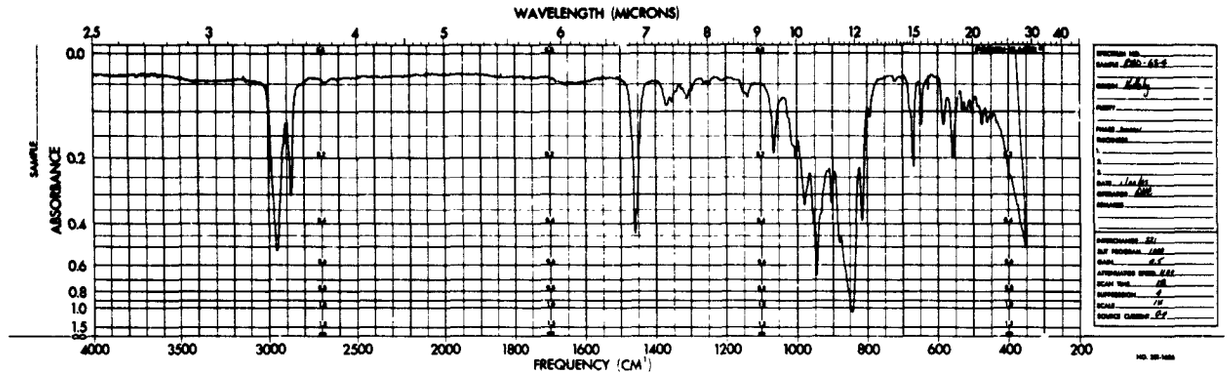


Figure 7. Infrared Spectrum of 1, 2-Bis(difluoramino)cyclohexane (cis- and trans- mixture)

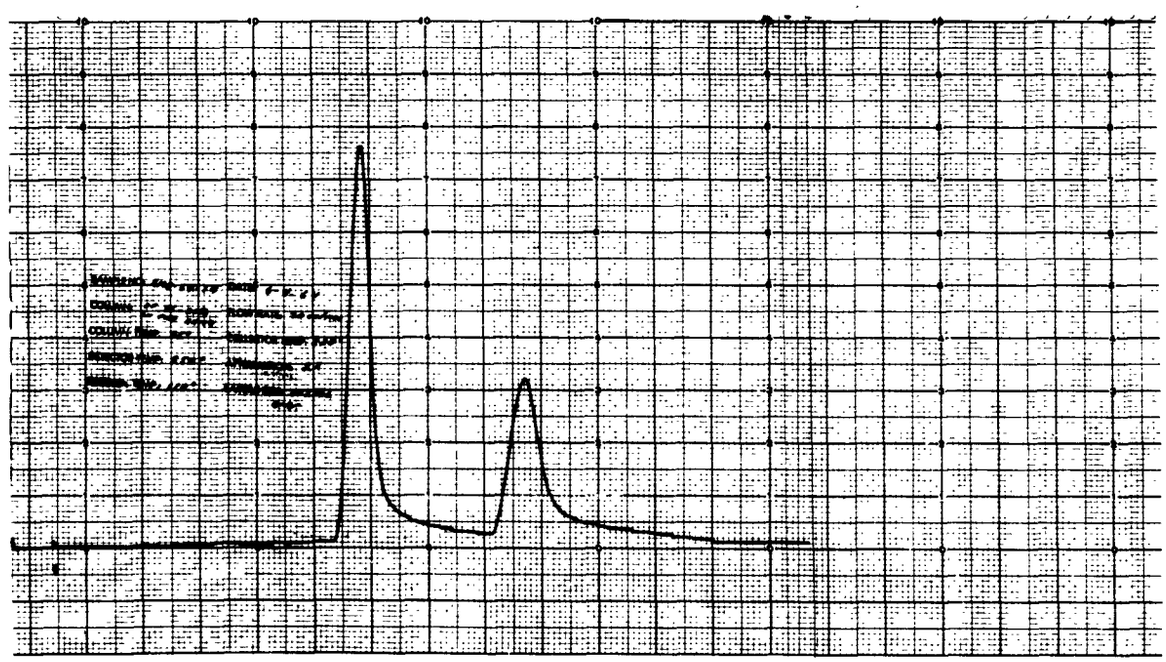


Figure 8. Gas Chromatogram of 1, 2-Bis(difluoramino)cyclohexane (cis- and trans- mixture)

F. METHYL 3,4-BIS(DIFLUORAMINO)BUTYRATE

3-Butenoic acid, b_9 65 to 68°C, n_D^{25} 1.4210, was converted to 3-butenoyl chloride by reaction with excess thionyl chloride (Ref 13). Treatment of the acid chloride with methanol (Ref 13) yielded methyl butene-3-oate, b_{750} 108°C, n_D^{25} 1.4048 (C.A. 49:3822d, b_{742} 107°C, n_D^{25} 1.4060). A solution of five gm (0.05 mole) of the ester in 15 ml methylene chloride was heated at 80°C overnight in a pressure reactor with 0.09 mole of N_2F_4, affording a 62 percent yield (average of five runs) of methyl 3,4-bis(difluoramino)butyrate, which, after gas chromatographic purification, had the following constants: $b_{1.5}$ 46.0°C, b_{760} 176.0°C, n_D^{25} 1.3870. The infrared spectrum and the chromatogram are shown in Figures 9 and 10, respectively.

Anal. Calcd. for $C_5F_4H_8N_2O_2$: C, 29.42; F, 37.23; H, 3.95; N, 13.72
Found : C, 29.46; F, 38.25 ± 1%; H, 4.04; N, 13.86

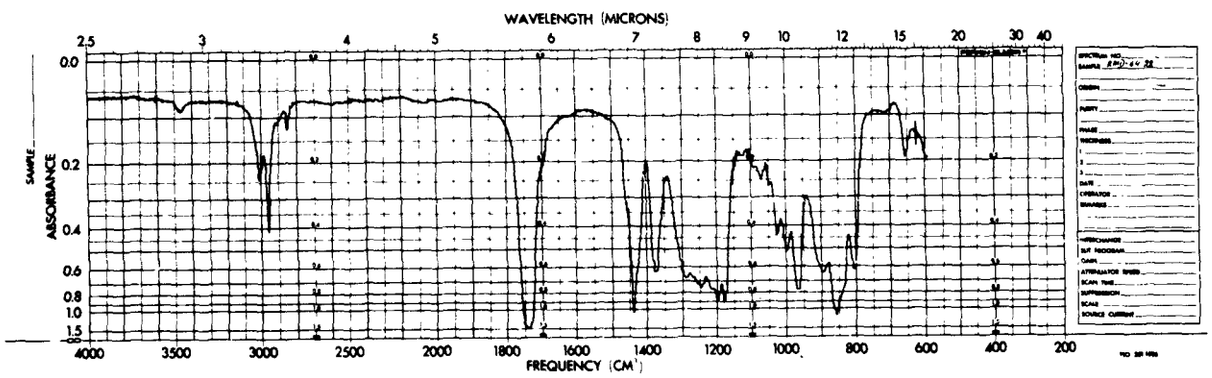


Figure 9. Infrared Spectrum of Methyl 3,4-Bis(difluoramino)butyrate

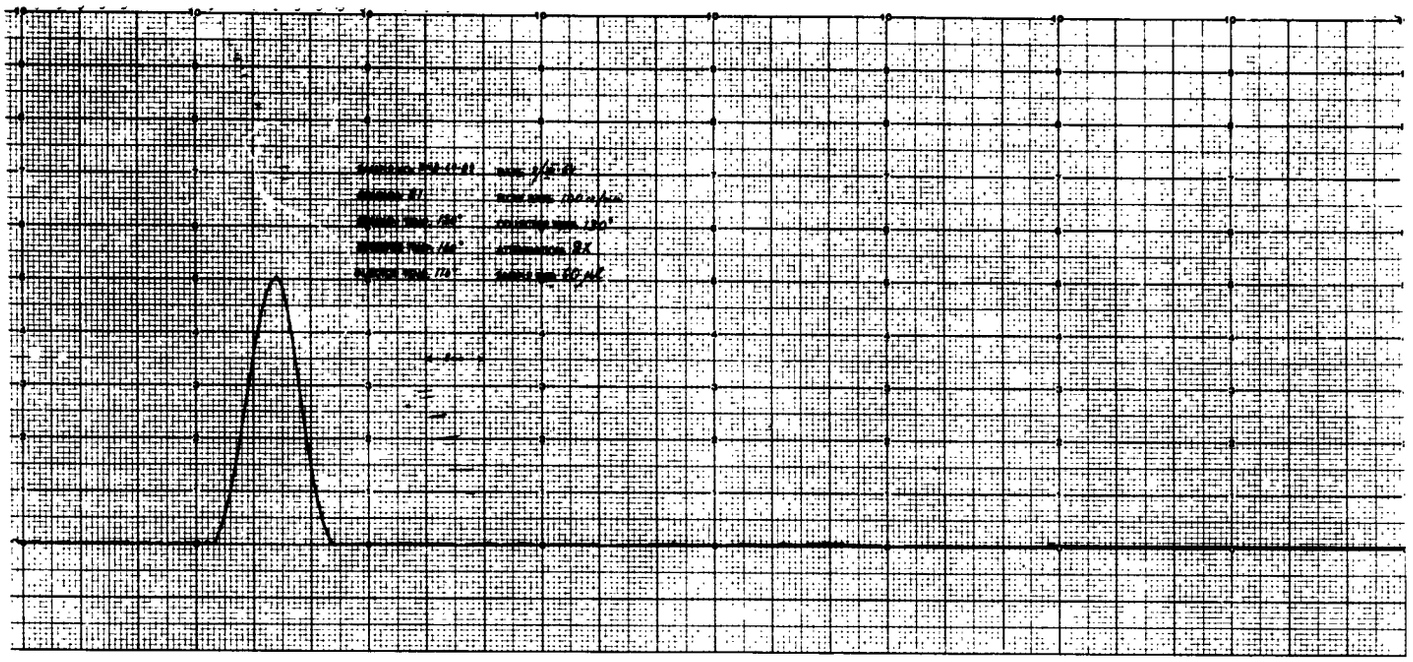


Figure 10. Gas Chromatogram of Methyl 3,4-Bis(difluoramino)butyrate

G. ETHYL 2,3-BIS(DIFLUORAMINO)PROPIONATE

Ethyl acrylate (five gm, 0.05 mole), b_{760} 98 to 99°C, was treated with N_2F_4 (2000 ml, 0.09 mole) under the same conditions as used in the synthesis of methyl 3,4-bis(difluoramino)butyrate. The yields of crude product varied from 67 to 85 percent. Work-up of the reaction product gave ethyl 2,3-bis-(difluoramino)propionate, which on gas chromatographic purification had the following constants: b_{20} 60.0°C, b_{760} 152.0°d, n_D^{25} 1.3745. The infrared spectrum and the chromatogram are shown in Figures 11 and 12, respectively.

Anal. Calcd. for $C_5F_4H_8N_2O_2$: C, 29.42; F, 37.23; H, 3.95; N, 13.72
Found : C, 29.34; F, 37.48; H, 4.06; N, 14.08

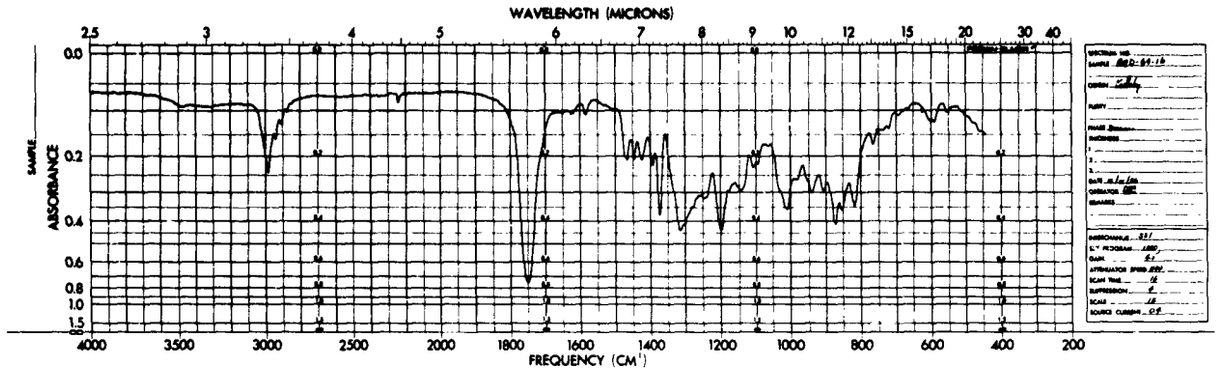


Figure 11. Infrared Spectrum of Ethyl 2, 3-Bis(difluoramino)propionate

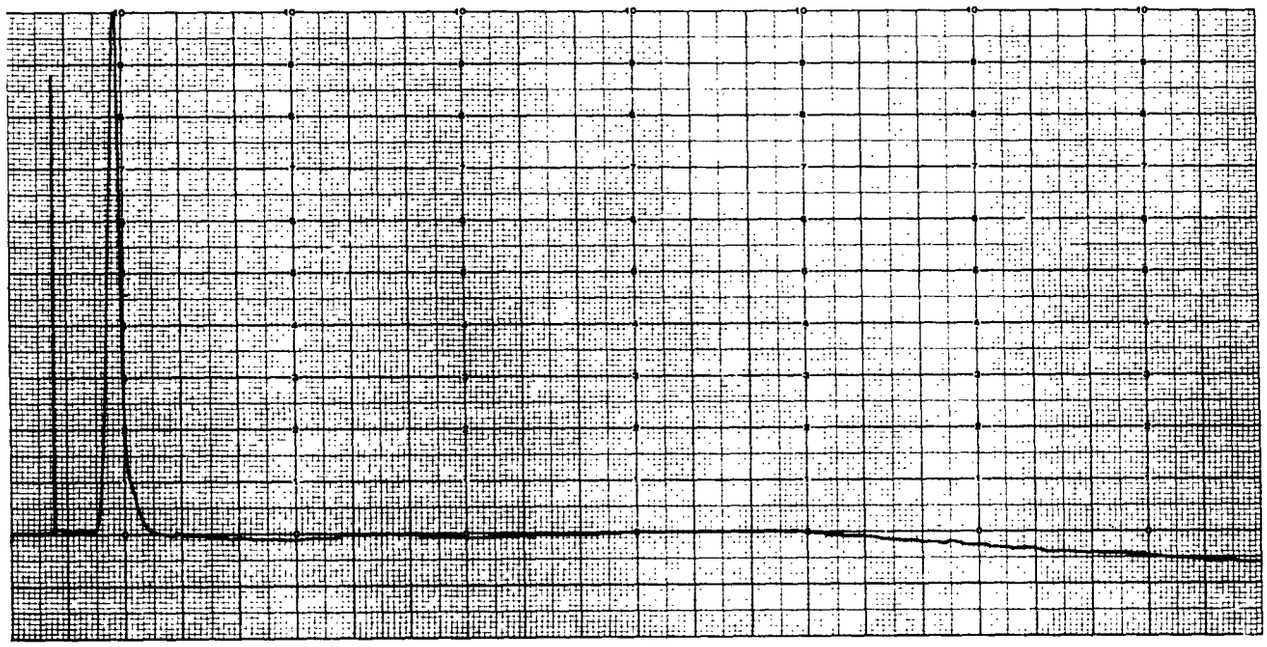


Figure 12. Gas Chromatogram of Ethyl 2, 3-Bis(difluoramino)propionate

This compound was found to be relatively heat sensitive. It underwent a partial decomposition of an inert column (F_2-passivated Cu column 12 foot by 3/8 inch, 20 percent Halocarbon Oil 14-25 on Fluoropak-80) at temperatures as low as 70°C. Under these conditions the degree of decomposition was reproducible as judged by a constant ratio of areas under peaks due to the ethyl 2, 3-bis(difluoramino)propionate and its decomposition product. Recycling gas chromatographically pure ester resulted in the appearance of a decomposition product with the same area under the peak and the same retention time. The nature of the decomposition product is presently being examined.

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Thiokol
REACTION MOTORS DIVISION

SECTION III

CHEMISTRY OF THE OXYGEN SUBFLORIDES

S. I. Morrow
A. R. Young, II

Report RMD 5043-64-F

RMD Project 5043, Task 53
Report Period: 1 January 1964 to
31 December 1964

Contract No. NOnr 4364(00)
ARPA Order No. 417
Project Code 4910

FOREWORD

This section of the report summarizes the results of studies of the chemistry of the oxygen subfluorides during the period from 1 January 1964 to 31 December 1964 under Navy Contract NOnr 4364(00), ARPA Order No. 417.

Personnel directly involved in these studies were: A. R. Young, II (Project Supervisor), S. I. Morrow (Principal Investigator), K. Tiger, J. Crothamel, and J. Dvorak. Analytical support was contributed by R. Storey, R. Crooker, D. Chowanec, A. Fremmer, and B. Fagan.

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I. INTRODUCTION

This research program represents a study of the chemistry of the oxygen subfluorides and of the stable salts of the dioxygenyl ion (O_2^+) that are derived from O_2F_2. It is hoped that the findings of this study will suggest routes to new inorganic oxidizers of potential value as propellant ingredients.

An investigation of the reaction of Xe with O_2F_2 led to the discovery of a new method for preparing XeF_2 in high yields and produced evidence suggesting the existence of new ternary compounds of xenon with oxygen and fluorine. These results are written in the form of a note which has been accepted for publication in Inorganic Chemistry and is presesented in Section II.

A discussion of incomplete work that will be continued during the next year and of exploratory reactions that gave negative results is presented in the appendix.

II. MANUSCRIPT OF PAPER FOR PUBLICATION

The Reaction of Xenon with Dioxygen Difluoride: A New Method for the Synthesis of Xenon Difluoride

[Accepted for Publication in Inorganic Chemistry]

[Contribution from the Chemistry Department, Reaction Motors Division, Thiokol Chemical Corporation, Denville, N.J.]

The Reaction of Xenon with Dioxygen Difluoride: A New Method for the Synthesis of Xenon Difluoride

by Scott I. Morrow and Archie R. Young, II

In the course of an investigation of the chemistry of dioxygen difluoride, we have examined its reactivity with xenon and with krypton at low temperatures. No reaction was observed with krypton up to -78°C, where O_2F_2 rapidly decomposes. Xenon, on the other hand, was converted quantitatively to a yellow solid by reaction with a large excess of O_2F_2 at -118°C. When this solid was sublimed at 50°C, high yields of xenon difluoride were obtained. The nature of the gases evolved during the process of warming the initial solid from -78°C to room temperature indicated the presence of unstable oxygen-containing compounds of xenon which we were unable to identify.

Experimental

Reaction of Dioxygen Difluoride with Xenon - The method of preparing dioxygen difluoride used in this work has been described by Streng.[1] The reagent was

(1) A. G. Streng, Chem. Rev., 63, 607 (1963).

generated at -196°C in a U-shaped Kel-F discharge tube and distilled at -78°C through a three-inch length of metal tubing (cooled with Dry Ice) to a Kel-F reaction tube maintained at -196°C. A measured quantity of xenon had previously been condensed into the bottom of the reaction tube. The xenon-dioxygen difluoride mixture was then warmed to -118°C (ethyl bromide slush bath) and held at that temperature for two hours. The temperature was measured with a low-temperature thermometer. The vapor pressure of dioxygen difluoride at -118°C is approximately 16 mm and that of xenon about 400 mm. In every experiment the xenon was virtually quantitatively converted to a yellow solid having a negligible vapor pressure up to -21°C. The excess dioxygen difluoride decomposed to oxygen and fluorine when the reactor and its contents were stored overnight at -78°C.

Purification of Xenon Difluoride - After the excess dioxygen difluoride had decomposed at -78°C and the decomposition gases were removed from the tube, the solid residue became white. Analysis of the gases recovered from the reactor never revealed more than trace quantities of xenon. The white solid was outgassed in a vacuum at -21°C for two to three hours. Volatile impurities removed by this treatment were CO_2, COF_2, CF_4, C_2F_6, SiF_4, and SF_6. (The latter four compounds are impurities in the fluorine, while COF_2 is commonly formed in small amounts in the preparation of the dioxygen difluoride.) The lower part of the evacuated Kel-F tube containing the white solid product was then immersed in a bath at 50°C. The upper part of the tube was cooled by wrapping it with a band of Pyrex wool which was kept saturated with acetone. Transparent crystals condensed on the cooler upper walls of the tube. Gases evolved during this process were composed of variable amounts of xenon, oxygen, and fluorine. A typical analysis of the off-gases obtained in this way was $Xe:O_2:F_2::2.8:1:1$. The crystals were removed from the tube in a dry box. They were identified as pure xenon difluoride by powder diffraction and single crystal x-ray analysis (a = 4.315, c = 6.990, space group 14/mmm).[2] A

(2) Single crystal analyses were carried out by W. Hamilton and J. Ibers at Brookhaven National Laboratories.

material balance for one experiment showed the yield of xenon difluoride was 98 percent of theory. In this run 4.25 mmoles of xenon was used. The amount of purified xenon difluoride obtained was 0.7052 gram (4.16 mmoles).

Evidence for Formation of an Oxygen-Containing Compound of Xenon - When the product, which had been out-gassed at -21°C, was recooled to -78°C, oxygen, xenon, and xenon difluoride appeared in its mass spectrometric fragmentation pattern. As the sample was warmed to -21°C, these same constituents, as well as traces of xenon tetrafluoride, appeared in the mass spectrometric pattern. When the sample was held at room temperature, the pattern consisted primarily of xenon difluoride with lesser amounts of xenon tetrafluoride and oxygen.

During sublimation of the product in a vacuum, significant amounts of xenon, oxygen, and fluorine were evolved. In one case when the solid product was heated to 49°C in a vacuum to recrystallize it, a mixture of Xe, O_2, and F_2 was evolved in a ratio of 2.7:1:1. In several experiments small amounts of a clear liquid were distilled from the solid products at room temperature *in vacuo*. These liquid distillates decomposed on standing for several hours at room temperature yielding mixtures of xenon, oxygen and fluorine. Determinations of the relative quantities of the components of the decomposition gases gave widely varying results from run to run.

It is interesting to note that Streng, et al.[3] have reported that significant yields of xenon oxyfluorides are obtained by the reaction of xenon with oxygen difluoride in an electric discharge, and by thermal reactions of xenon with oxygen difluoride or oxygen-fluorine mixtures. The stabilities of the oxygenated products obtained from oxygen difluoride are apparently much greater than observed for the products obtained in this study.

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(3) A. G. Streng, A. D. Kirshenbaum, L. V. Streng, and A. V. Grosse, Noble-Gas Compounds, H. Hyman, Ed., University of Chicago Press, 1963, p. 77.

Acknowledgement - This work was supported by the Advanced Research Projects Agency and monitored by the Office of Naval Research under Contract NOnr 4364(00).

III. APPENDIX — INORGANIC CHEMISTRY OF OXYGEN SUBFLUORIDES AND DIOXYGENYL SALTS

A. INTRODUCTION

The work described in this section of the report is a continuation of studies of the chemistry of O_2AsF_6, the characterization of which has been reported previously (Ref 1 and 2), and of O_2F_2. Some preliminary studies carried out with O_3F_2 are also included. During the past year RMD was primarily concerned with pursuing those reactions of O_2AsF_6 and of O_2F_2 that might lead to new stable oxidizer structures. Reactions clearly showing no promise of yielding this result were not studied exhaustively and, consequently, not completely characterized. Some encouraging results have been obtained in the efforts to prepare dioxygenyl perchlorate (O_2ClO_4) by metathesis from O_2AsF_6. Further studies pertaining to the possible existence of O_2ClO_4 will be carried on during the next year's program.

B. CHEMISTRY OF DIOXYGENYL SALTS

The characterization of the dioxygenyl salts, O_2PF_6, O_2AsF_6, and O_2SbF_6 has been reported previously (Ref 1). In attempts to examine the chemical properties of dioxygenyl salts, we have wo ed almost exclusively with O_2AsF_6. The phosphorous compound is not stable at room temperature and the antimony compound is less convenient to prepare and purify because of the low volatility of SbF_5.

The study of the chemistry of O_2AsF_6 was limited to two general reactions that were believed to be capable of producing interesting new oxidizer structures, namely: (a) reactions of O_2AsF_6 with perchlorates and compounds of other oxidizing anions, and (b) reactions of O_2AsF_6 with radicals, in order to form coupling products with the paramagnetic dioxygenyl ion. Evidence has been obtained that O_2AsF_6 undergoes exchange reactions with perchlorates both in solution and in the solid state, but the anticipated product of such an exchange, O_2ClO_4, has not as yet been isolated.

1. Structure of O_2AsF_6

The powder diffraction pattern of O_2AsF_6 has been indexed on a cubic unit cell having an 8.00 Å edge (Ref 1). It was also determined that $NO^+AsF_6^-$ has an identical powder diffraction pattern, a fact which strongly supports an ionic structure for O_2AsF_6. During the past year, we sent several grams of O_2AsF_6 to Dr. W. C. Hamilton of Brookhaven National Laboratories for the purpose of determining the structural parameters of O_2AsF_6 by neutron diffraction analysis. Some difficulty has been encountered in selecting the proper material to use as a sample holder for this reactive compound, and the neutron diffraction studies are incomplete at present. The data obtained so far, however, confirm our assignment of a cubic unit cell (a = 8.00Å) to O_2AsF_6.

We recently observed that O_2AsF_6 forms stable solutions in IF_5 and hopes shortly to obtain an F^{19} NMR spectrum of an IF_5 solution. It is hoped that the fluorine on arsenic resonance peaks will be observable in IF_5.

2. Stability of O_2AsF_6 Solutions

Since ionic substitution reactions are most conveniently carried out in solution, we examined the compatibility of O_2AsF_6 with a variety of potential reaction media. Iodine pentafluoride was the only solvent examined from which O_2AsF_6 could be recovered at room temperature. The observations made on attempting to form solutions of O_2AsF_6 in IF_5, HF, AsF_3, and $HClO_4$ are presented in the following discussion.

a. Iodine Pentafluoride

Reagent grade IF_5 was further purified by bubbling a mixture of fluorine and nitrogen through it until it became colorless, and then distilling the IF_5 in a glass apparatus under vacuum. The colorless liquid was collected in glass receivers, which were then sealed off in a vacuum and kept at -78°C until used. Samples of O_2AsF_6 dissolved readily in solvent prepared in this manner. Although small amounts of gases may have evolved from these solutions on standing at room temperature, most of the O_2AsF_6 could be recovered unchanged by distilling off the IF_5. The residual solid was identified by x-ray diffraction.

b. Hydrogen Fluoride

Previous work with O_2AsF_6 and HF resulted in the formation of a purple solution, which began to give off O_2 at about -50°C (Ref 2). Reinvestigation

of this reaction in a system free from brass or copper showed that O_2AsF_6 solutions in HF are actually colorless. Evidently the distillation of HF through copper introduces an impurity that imparts a purple color to the solution. It was found that the colorless HF solutions were stable up to -20°C where vigorous gas evolution occurred. Anhydrous reagent HF contains traces of moisture, according to Jarry (Ref 3). If the solvent were rigorously purified as he describes it, it is possible that the stability of this system would be further improved. This is a matter of practical consequence since it might be possible to evaluate reactions of O_2AsF_6 in HF at normal temperatures.

c. Arsenic Trifluoride

The O_2AsF_6-AsF_3 system was evaluated at -10°C. O_2AsF_6 dissolved completely in the liquid AsF_3, but as the mixture was allowed to stand during a two-hour period, oxygen was evolved. The amount given off was approximately equal to the dioxygenyl content of the O_2AsF_6 used. When the AsF_3 was distilled off at 25°C in a vacuum, only a trace of white solid was left behind. Some of the AsF_3 was evidently fluorinated to AsF_5 by O_2AsF_6.

d. Anhydrous Perchloric Acid

Anhydrous perchloric acid was obtained by distilling 70 percent perchloric acid from P_2O_5. It was thought that O_2AsF_6 might either form stable solutions in $HClO_4$ or react as shown in equation 1 to give a solution of O_2ClO_4.

$$O_2AsF_6 + (xs)HClO_4 \not\longrightarrow HF + AsF_5 + O_2ClO_4 \qquad (1)$$

The anhydrous $HClO_4$ was distilled onto a sample of O_2AsF_6 at -196°C. The system was allowed to warm to room temperature, and a vigorous reaction was observed at the melting point of $HClO_4$ (-112°C). The nature of the gases evolved was not determined, but upon removal of the solvent only a trace of solid residue remained, so it is assumed that the dioxygenyl ion was destroyed.

3. Attempted Synthesis of Dioxygenyl Perchlorate

A Born-Haber cycle calculation indicates that the heat of formation of dioxygenyl perchlorate (O_2ClO_4) is +6.4 kcal/mole. The calculation involves two assumptions, namely: (a) that O_2ClO_4 would be an ionic solid, and (b) that it would be isomorphous with $NOClO_4$ and, therefore, have the same lattice

energy. The lattice energy of a salt, U_{MX}, is defined as the internal energy change (ΔE) for the reaction shown in equation 2. The lattice energy is related

$$MX(s) \xrightarrow{\Delta H} M^+(g) + X^-(g); \; \Delta H = U_{MX} + 2RT \qquad (2)$$

to the heats of formation of the gaseous ions M^+ and X^- and the heat of formation of the solid MX by equation 3. If the lattice energy is known, then ΔH_{MX} may

$$U_{MX} = \Delta H_{M^+} + \Delta H_{X^-} - (\Delta H_{MX} + 2RT) \qquad (3)$$

be calculated, and conversely, if the heat of formation of a salt is known, its lattice energy can be determined. In our calculation it was assumed that $U_{O_2ClO_4} = U_{NOClO_4}$. Since O_2AsF_6 is known to be isomorphous with $NOAsF_6$ (Ref 1), this seemed a reasonable assumption. The lattice energy of $NOClO_4$ was determined to be 195 kcal/mole using the following constants:

ΔH_{NOClO_4}	= -41.79 kcal/mole (Ref 4)
ΔH_{NO}	= 21.6 kcal/mole (Ref 5)
I_{NO} (Ionization Potential)	= 213.3 kcal/mole (Ref 6)
$\Delta H_{ClO_4^-}$	= -80.5 kcal/mole (Ref 7)

Using 195 kcal/mole as the lattice energy of O_2ClO_4 and 283.1 kcal/mole as the heat of formation of $O_2^+(g)$ (Ref 5), the heat of formation of O_2ClO_4 is obtained from equation 3. The value of +6.4 kcal/mole for O_2ClO_4 predicts a greater thermodynamic stability for it than for known compounds of chlorine and oxygen:

ΔH_{ClO_2}	= +24.7 kcal/mole
ΔH_{Cl_2O}	= +18.2 kcal/mole
$\Delta H_{Cl_2O_7}$	= +63.4 kcal/mole

In view of this, it is believed that efforts to synthesize O_2ClO_4 are well justified. RMD has attempted the synthesis of O_2ClO_4 from O_2AsF_6 by reactions with $HClO_4$ (equation 1), Cl_2O_7 (equation 4), $KClO_4$ in IF_5 (equation 5), and NO_2ClO_4 in the absence of solvent (equation 6).

$$O_2AsF_6 + Cl_2O_7 \not\longrightarrow O_2ClO_4 + ClO_3AsF_6 \qquad (4)$$

$$O_2AsF_6 + KClO_4 \xrightarrow[IF_5]{?} O_2ClO_4 + KAsF_6 \qquad (5)$$

$$O_2AsF_6 + NO_2ClO_4 \xrightarrow{?} O_2ClO_4 + NO_2AsF_6 \qquad (6)$$

a. Reaction of O_2AsF_6 with Cl_2O_7

O_2AsF_6 reacted slowly with Cl_2O_7 at -78°C to give gaseous products. Perchloryl fluoride, chloryl fluoride, oxygen, and chlorine were identified in the gas phase by mass spectroscopy. After removal of all volatile components, the residual solid was examined by x-ray diffraction and identified as unreacted O_2AsF_6.

b. Reaction of O_2AsF_6 with $KClO_4$ in IF_5

The addition of O_2AsF_6 to a slightly colored solution of $KClO_4$ in IF_5 initially produced a vigorous evolution of gases. This initial reaction was apparently only a reaction with the colored impurity (I_2 or IF) in the IF_5, because it ceased as soon as the color was discharged. After this, only very slow gas evolution was observed. The solid recovered from the IF_5 solution showed only x-ray diffraction lines due to $KAsF_6$. Since this is the anticipated byproduct of the desired metathesis (equation 5), it is possible that the slow gas evolution observed was caused by decomposition of O_2ClO_4. In further studies of the reaction of perchlorates with O_2AsF_6 in IF_5, the nature of the starting perchlorate (i.e. $CsClO_4$, $AgClO_4$) will be varied in the hope that an insoluble hexafluoroarsenate will form. This will permit rapid separation of O_2ClO_4 from the $MAsF_6$ byproduct and the IF_5 solvent. It is possible that $KAsF_6$ catalyzed the decomposition of O_2ClO_4 in the experiment described.

4. Reaction of O_2AsF_6 with NO_2ClO_4

During the work of the preceding year (Ref 1) an attempt was made to carry out a metathesis between O_2AsF_6 and NO_2ClO_4 below -20°C in anhydrous HF. It appeared that no reaction occurred on mixing the solids, but as soon as liquid HF (-78°C) was added to the solid mixture a vigorous reaction ensued, liberating oxygen and perchloryl fluoride.

We have recently reinvestigated the O_2AsF_6-NO_2ClO_4 system in the absence of a solvent, and the results show that reaction does occur in the solid state. In several experiments (Table I) conducted at temperatures ranging from -78°C to room temperature, x-ray data (Figure 1) indicate the conversion of NO_2ClO_4 to NO_2AsF_6. In addition, there are strong diffraction lines present at approximately 4.91 Å and 4.53 Å, which do not belong to O_2AsF_6, NO_2AsF_6, NO_2ClO_4, or $NOClO_4$ (a possible impurity in NO_2ClO_4). These, together with weak lines at 2.90 Å and 1.77 Å (Runs No. 1, 2, and 3), appear to be associated with a single unknown solid phase formed in all three of these experiments. When one considers the presence of these unknown diffraction lines and the presence of NO_2AsF_6 (major line at 3.53 Å), as well as the absence of major lines of NO_2ClO_4 or O_2AsF_6, the existence of O_2ClO_4 is strongly suggested.

In all the runs except No. 2 (Table I and Figure 1) a color change to orange or yellow occurred on agitating the two white solid reagents for periods of one to three hours. Nevertheless, it cannot be concluded that the orange color is to be associated with O_2ClO_4, because Run No. 2, in which there was no color change, also gave NO_2AsF_6 and the unknown solid phase having diffraction lines at 4.91 Å and 4.53 Å. It is possible that the orange color is caused by the presence of oxides of chlorine.

There is some uncertainty about whether the chlorine containing gaseous product observed in several runs was Cl_2O_7 or ClO_3F, since the infrared spectra of these two compounds are quite similar. In no case did the amount of oxygen liberated approach the oxygen content of the initial dioxygenyl hexafluoroarsenate.

It appears that the results of these experiments offer some promise of the existence of O_2ClO_4, but additional evidence is needed to substantiate such a claim.

TABLE I

REACTION OF NO_2ClO_4 WITH O_2AsF_6

Run No.	Ratio of Reagents	Temp (°C)	Solvent	Products: Gaseous	Products: Solid	Comments
1	1:1	27	None	Not examined	NO_2AsF_6 + Unknown A*	Color change, white → orange
2	1:1	-78	C_3F_8 (suspension)	Not examined	NO_2AsF_6 + Unknown A*	No color change
3	1:1	-78 → 27	None	O_2, ClO_3F or Cl_2O_7	NO_2AsF_6 + Unknown A*	Color change, white → yellow
4	1:1	-78	C_3F_8 (suspension)	Negligible	NO_2AsF_6 + $NOClO_4$, Unknown A*	Color change, white → yellow
5	1:1	27	None	O_2, ClO_3F or Cl_2O_7	NO_2ClO_4	Color change, white → orange
6	1	0	None	Not examined	Unknown B**	Color change, white → yellow

*Unknown A is associated with x-ray diffraction lines at 4.91 Å, 4.53 Å, 2.90 Å, 1.77 Å (Figure 1)

**Unknown B is associated with x-ray diffraction lines at 4.94 Å, 3.16 Å, 3.00 Å, (Figure 1)

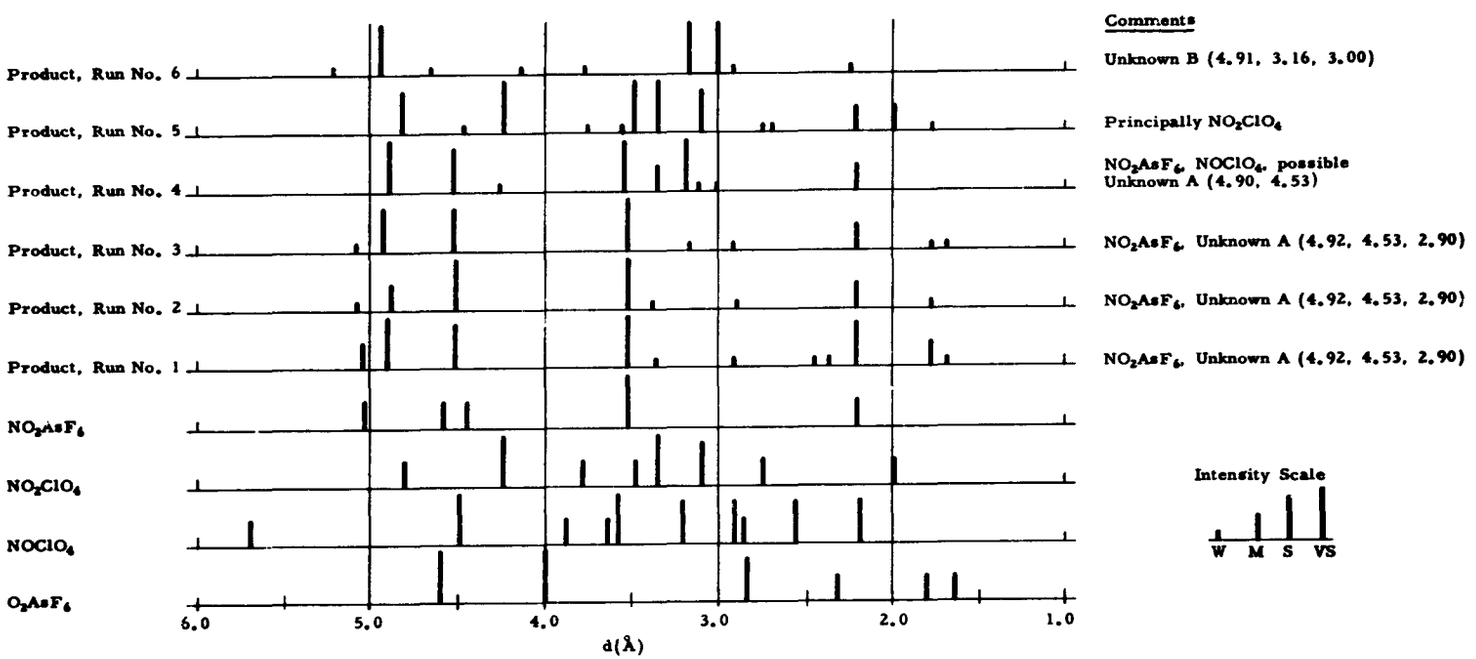

Figure 1. Diffraction Patterns of O_2AsF_6-NO_2ClO_4 Reaction Products

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5. Other Reactions of Dioxygenyl Hexafluoroarsenate

a. Reaction of O_2AsF_6 with Nitroform

The dioxygenyl salt of nitroform should be a very powerful oxidizer and might be prepared according to equation 7.

$$O_2AsF_6 + HC(NO_2)_3 \xrightarrow{HF} HF\uparrow + AsF_5\uparrow + O_2^+C(NO_2^-)_3 \qquad (7)$$

When solutions of nitroform and O_2AsF_6 in HF were mixed at -78°C, vigorous gas evolution occurred. This gas was identified as oxygen. In a separate experiment it was found that O_2AsF_6 does not evolve oxygen at a rapid rate in HF until the temperature is as high as -20°C. A white precipitate remained when the solvent was removed by vacuum distillation. Nitrogen oxides were also found in the gases from the reaction. The solid residue became liquid during storage prior to analysis. Its infrared spectrum showed a weak -OH stretching frequency and broad bands throughout the observed range, as well as the AsF_6^- ion absorption. The rapid evolution of oxygen at -78°C in this experiment indicates that $O_2C(NO_2)_3$ cannot be prepared in HF.

b. Reaction of O_2AsF_6 with SO_2Cl_2

Studies of the reaction of O_2AsF_6 with SO_2Cl_2, as well as with unsaturated carbon compounds, showed the power of this material as a fluorinating agent (Ref 1). Although SO_2Cl_2 is very difficult to fluorinate, the following reaction has been observed:

$$SO_2Cl_2 + O_2AsF_6(xs) \xrightarrow{25^\circ C} SO_2F_2 + O_2 + \text{-------} \qquad (8)$$

It is believed that O_2AsF_6 acts as follows, releasing fluorine atoms which are very active fluorinating species:

$$O_2AsF_6 \longrightarrow [O_2F\cdot] + AsF_5$$
$$[O_2F\cdot] \longrightarrow O_2 + F\cdot \qquad (9)$$

An attempt was made to continue the fluorination of SO_2Cl_2 to the fluoroxy compounds, $F_3\underset{\underset{O}{\|}}{S}OF$ and $F_4S(OF)_2$, but no attack on the S=O bond could be effected by the use of a large excess of O_2AsF_6 and longer reaction periods.

c. Reaction of O_2AsF_6 with BrF_5

It was hoped that O_2AsF_6 might be a sufficiently powerful fluorinating agent to convert the known interhalogen, BrF_5 to the as-yet-unreported heptafluoride, BrF_7 (equation 10). BrF_5 was condensed into O_2AsF_6 at -196°C

$$BrF_5 + 2O_2AsF_6 \xrightarrow{?} BrF_7 + 2O_2 + 2AsF_5 \qquad (10)$$

and allowed to warm slowly to room temperature. A purple color appeared on the surface of the O_2AsF_6 during this process, a possible indication of complex formation. The color did not persist up to room temperature, however, and noncondensable (at -196°C) gases were formed. These were shown to be oxygen and fluorine. The condensable fraction of the gaseous products contained BrF_5, AsF_5, possibly some AsF_3, and impurities present originally in the BrF_5 reagent (BF_3, SiF_4, fluorocarbons). The presence of oxygen in the gaseous products indicates that the dioxygenyl salt interacted in some manner with BrF_5. Since no higher fluoride of bromine was isolated, the overall effect of the reaction was simply decomposition of O_2AsF_6.

d. Attempted Reaction of O_2AsF_6 with the Difluoramine Radical ($\cdot NF_2$)

The dioxygenyl ion is an odd electron species potentially capable of coupling with other radicals, possibly as shown in equation 11. Several attempts were

$$\cdot O_2^+ + \cdot NF_2 \longrightarrow F_2NO_2^+ \qquad (11)$$

made to form $F_2NO_2^+AsF_6^-$ by condensing $\cdot NF_2$ radicals onto O_2AsF_6 at -196°C. The $\cdot NF_2$ radicals were generated by flowing N_2F_4 through a Monel tube at 300°C. The only solid product isolated at room temperature by this technique was NO_2AsF_6 and possibly $NOAsF_6$, which is indistinguishable from O_2AsF_6 by x-ray. NO_2AsF_6 and $NOAsF_6$ are reasonable end products of the decomposition of a species such as $NF_2O_2^+AsF_6$. In addition to noncondensable gases (O_2 and F_2), various nitrogen-containing gaseous products were obtained in small quantities, including NF_3, NOF, and NO_3F.

It is highly likely that the recombination of $\cdot NF_2$ radicals is so rapid at -196°C that little if any contact of O_2AsF_6 with $\cdot NF_2$ was effected in these experiments. Further study of the proposed coupling of $\cdot NF_2$ with O_2^+ (equation 11) will be undertaken using an irradiation technique to generate the radicals at liquid nitrogen temperatures, and low temperature infrared examination to detect products.

C. CHEMISTRY OF O_2F_2 AND O_3F_2

The reaction of dioxygen difluoride with xenon is described in an earlier section of this report (Task 52) This reaction occurs at −118°C with quantitative conversion of xenon to the difluoride and unstable oxyfluorides The reaction chemistry of O_2F_2 was studied further with the objective of utilizing its high reactivity to prepare new halogen fluorides, oxyfluorides, and oxidizing anions. Exploratory studies were made of some reactions of O_3F_2 but no marked differences in reactivity of products observed with O_2F_2 have been observed to date.

1. Reactions of Dioxygen Difluoride

In attempts to uncover reactions leading to new oxidizers, we investigated reactions of O_2F_2 with the inorganic halogen-containing compounds shown in the following hypothetical equations:

$$O_2F_2 + CsCl \xrightarrow{?} CsF + [FClOO] \longrightarrow Cs^+ClO_2F_2^- \qquad (12)$$

$$O_2F_2 + BrF_5 \xrightarrow{?} O_2 + BrF_7 \qquad (13)$$

$$\xrightarrow{?} O_2BrF_6 + 1/2F_2 \qquad (14)$$

$$O_2F_2 + CsBrF_6 \xrightarrow{?} CsF + BrF_7 + O_2 \qquad (15)$$

$$O_2F_2 + CsClF_4 \xrightarrow{?} CsClF_6 + O_2 \qquad (16)$$

$$O_2F_2 + ClOAsF_5 \longrightarrow ClOF + O_2AsF_6 \qquad (17)$$

$$2O_2F_2 + ClOAsF_5 \longrightarrow F_2ClOAsF_6 + 2O_2 + 1/2F_2 \qquad (18)$$

The results of these experiments are discussed in the following paragraphs.

a. Reaction of O_2F_2 with CsCl

A series of seven experiments were conducted in a study of the reaction of O_2F_2 and CsCl (Table II) in attempts to isolate and characterize what appeared to be a solid product containing active fluorine. Chemical analysis of solid products from two experiments (No. 1 and 4, Table III), corresponded to a hypothetical composition, $CsClO_2F \cdot CsF$ (Cs:Cl:F:O=1:0.5:1:1). In support of the presence of such an anion (ClO_2F^-) it was observed that the solid product attacked glass. X-ray patterns obtained on samples sealed in Pyrex capillaries were found to be identical to the pattern exhibited by Cs_2SiF_6. On the other hand, aqueous solutions of the solid were only weakly oxidizing toward KI.

Infrared spectra of the O_2F_2-CsCl product (Figures 2 and 3) shed little light on the composition of the material. These spectra were obtained on a KBr pellet (Figure 2) and by mulling the solid in a Kel-F oil (Figure 3). Both show strong absorptions at approximately 1235 cm^{-1} and between 1400-1550 cm^{-1}, which are the regions of absorption of NO_2^- and NO_3^- ions. However, qualitative tests showed the absence of significant nitrate and nitrite impurities. The spectrum shown in Figure 3 has an absorption at 725 cm^{-1} attributable to $SiF_6^=$. The presence of this band was found to be caused by the reaction of the sample with a Pyrex vial in which it was stored prior to infrared analysis. When the solid was not allowed to contact glass, the band at 725 cm^{-1} did not appear (Figure 2).

Experiment 7 was made in an attempt to determine conclusively whether a new oxidizing anion was present in the solid product of the CsCl-O_2F_2 reaction. Considerable efforts were taken to exclude impurities and to drive the reaction as nearly to completion as possible by repeatedly treating the CsCl with excess O_2F_2 at -110 and then at -78°C. When a portion of the solid product was hydrolyzed in a vacuum, no gases were evolved. Results of chemical analysis of the hydrolysate are given in Table III, and are quite similar to previous results (Cs:Cl:F = 1:0.5:0.9). When the hydrolysate was tested for oxidizing power with acidic KI solution, it was found to have negligible activity. The type of anion we have been proposing as the product ($FClOO^-$) would be expected to either form strongly-oxidizing aqueous solutions, or to liberate oxygen and/or

TABLE II

REACTIONS OF O_2F_2 WITH CsCl

Experiment Number	CsCl (gm)	Diluent	Temperature (°C)	Product (gm)	Color of Product
1	0.5736	none	-110 to -78	0.6075	white
2	2.4171	none	-110 to -78	2.4330	yellow
3	1.6494	C_3F_8	-110 to -78	1 7514[a]	yellow
4	0.6257[a]	C_3F_8	-78	0.6212	yellow
5	0.6260	none	-106 to -78	0.6383	yellow
6	0.9750	none	-100	b	b
7	---	none	-110 to -78	1.1145	yellow

a - Some of the product from experiment 3 was ground and used in experiment 4

b - Abandoned because of experimental difficulty

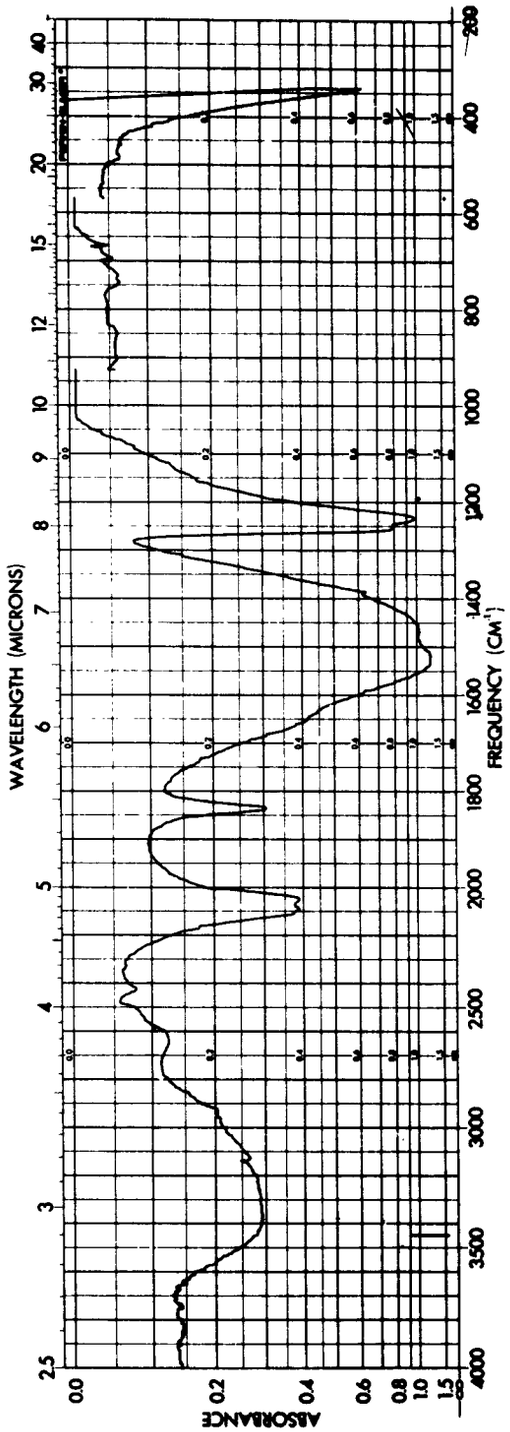

Figure 2. Infrared Spectrum of O_2F_2-CsCl Product (KBr Pellet)

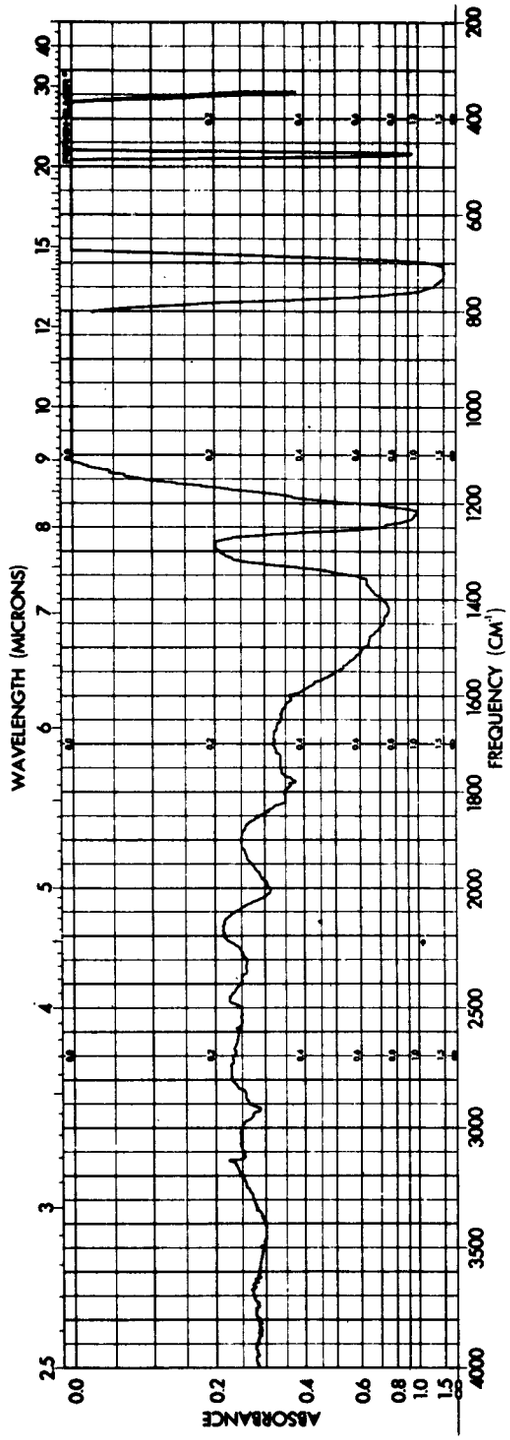

Figure 3. Infrared Spectrum of O_2F_2-CsCl Product (Kel-F Mull)

TABLE III

ELEMENTAL COMPOSITION OF O_2F_2-CsCl SOLID PRODUCT

Element (%)	Found: CsCl Reagent	Found: Product Run No. 1	Found: Product Run No. 4	Found: Product Run No. 7	Calculated for: CsCl	Calculated for: CsF	Calculated for: Cs_2O	Calculated for: $CsClO_2F$:CsF
Cs	79.22	67.54	71.34	75.15	78.92	87.50	94.32	71.59
Cl	21.42	8.84	8.75	10.1	21.08	---	---	9.56
F	---	10.60	11.60	9.25	---	12.50	---	10.23
O	---	13.02*	8.31*	5.50*	---	---	5.68	8.62
Atomic Ratios	Cs:Cl 1:1	a	b	c	Cs:Cl 1:1	Cs:F 1:1	Cs:O 1:2	Cs:Cl:F:O 1:0.5: 1:1

*By difference

a - Cs:Cl:F:O
1:0.5:1.1:1.6

b - Cs:Cl:F:O
1:0.5:1.1:1

c - Cs:Cl:F:O
1:0.5:0.9:0.6

OF_2 by hydrolysis. Since neither of these properties were observed it is concluded that the product must be a mixture of CsF and CsCl. If one adds the values assigned to oxygen content (obtained by difference) in Table III to those found for cesium content, one obtains for percent Cs: 80.56, 79.65, and 80.65, respectively. These values are not only internally consistent but are intermediate between calculated cesium contents for pure CsCl (78.92) and pure CsF (87.50), as would be expected for a mixture. It is quite possible then, that the cesium determinations have been low and there is little or no oxygen in the products. The reaction of O_2F_2 with CsCl in all probability involves a simple fluorination (equation 19). The observed yellow color and

$$O_2F_2 + 2CsCl \longrightarrow 2CsF + Cl_2 + O_2 \qquad (19)$$

weak oxidizing activity of the product may be caused by adsorbed chlorine. No further work with this reaction is contemplated.

b. Attempted Reaction of O_2F_2 with BrF_5

The action of O_2F_2 on BrF_5 was investigated as a possible route to a new interhalogen oxidizer, BrF_7, or to the dioxygenyl salt, O_2BrF_6. Excess O_2F_2 was distilled onto BrF_5 at -196°C and the system was allowed to warm slowly to -78°C where it remained until a constant pressure was obtained. No volatile products other than oxygen and fluorine were detected, and upon removal of the BrF_5 no solid residue was apparent.

c. Attempted Reaction of $CsBrF_6$ with O_2F_2

An alternate approach to BrF_7 might be to fluorinate a BrF_6^- salt. The low temperatures at which O_2F_2 releases active fluorine should make this an ideal reagent for the preparation of BrF_7. The preparation of $CsBrF_6$ was attempted by heating CsF and BrF_5 to 140°C in a Monel cylinder for several hours. Since the loss of BrF_5 indicated conversion to the desired product, a sample of the solid recovered from the cylinder was treated with O_2F_2 at -78°C. The material obtained after the reaction was identified by x-ray analysis as $CsBrF_6$.

Subsequent x-ray analysis of the solid starting material used in the O_2F_2 reaction showed that it was not, in fact, $CsBrF_6$. It is believed that the initial

product of the high temperature $CsF\text{-}BrF_5$ reaction was $CsBrF_4$ which was converted to $CsBrF_6$ as shown in equation 20. The $CsBrF_6$ was then subjected to

$$O_2F_2 + CsBrF_4 \longrightarrow CsBrF_6 + O_2 \qquad (20)$$

repeated contact with freshly-prepared O_2F_2 at -78°C without any evidence of further reaction.

d. Attempted Reaction of O_2F_2 with $CsClF_4$

The reaction between $CsClF_4$ and O_2F_2 was investigated to determine whether the ClF_6^- ion might be prepared (equation 21). $CsClF_4$ was allowed to contact successive samples of freshly-generated O_2F_2 over a period of several hours. No change in the x-ray pattern of the $CsClF_4$ was detected after this treatment.

$$O_2F_2 + CsClF_4 \not\longrightarrow O_2 + CsClF_6 \qquad (21)$$

e. Reaction of O_2F_2 with $ClO\cdot AsF_5$

Schmeisser and Brandle have reported the synthesis of a 1:1 adduct of Cl_2O with AsF_5 (Ref 8). The adduct decomposes at -50°C to give Cl_2 and $ClO\cdot AsF_5$ (equation 22). No information is available about the stability of

$$Cl_2O + AsF_5 \xrightarrow{-78^\circ C} Cl_2O\cdot AsF_5 \xrightarrow{-50^\circ C} 1/2Cl_2 + ClO\cdot AsF_5 \qquad (22)$$

$ClO\cdot AsF_5$, but it reacts with NO_2 to give chlorine nitrate as shown in equation 23. This adduct of chlorine monoxide might yield some interesting products

$$ClO\cdot AsF_5 + NO_2 \longrightarrow ClO\text{-}NO_2 + AsF_5 \qquad (23)$$

upon reaction with O_2F_2. One possibility is the formation of FClO (or ClOF) during the formation of O_2AsF_6, as shown in equation 17. On the other hand, O_2F_2 might act simply as a fluorinating agent, yielding $F_2ClO^+AsF_6^-$ (equation 18) from which one might obtain F_3ClO.

In view of these interesting possibilities, Cl_2O was prepared by the action of Cl_2 on yellow mercuric oxide suspended in Freon 112 (equation 24) and

$$2Cl_2 + 2HgO \longrightarrow Cl_2O + HgCl_2\cdot HgO \qquad (24)$$

treated with AsF_5 at -78°C in Freon 112. The $Cl_2O \cdot AsF_5$ was obtained as an insoluble white solid, and after removal of Freon at -50°C, the remaining solid ($ClO \cdot AsF_5$) was treated repeatedly with freshly-generated O_2F_2. The solid reagent underwent a color change to purple upon contact with liquid O_2F_2 at -160°C. The known volatile products of this reaction were Cl_2, O_2, F_2, and ClO_3F. In addition, there were obtained a liquid and a solid residue (at room temperature) the identities of which have not as yet been determined.

f. Reaction of O_2F_2 with Cl_2O_7

As part of the effort to prepare $O_2^+ClO_4^-$ the following reaction was attempted:

$$Cl_2O_7 + O_2F_2 \not\longrightarrow O_2ClO_4 + ClO_3F + 1/2F_2 \qquad (25)$$

When O_2F_2 and freshly-prepared Cl_2O_7 were allowed to react at -78°C, the only products detected were ClO_3F and noncondensable gases (O_2, F_2).

g. Reaction of O_2F_2 with $KC(NO_2)_3$

The reaction of O_2F_2 with potassium nitroform (equation 26) was investigated as another possible route to dioxygenyl salts containing energetic oxidizing

$$O_2F_2 + KC(NO_2)_3 \not\longrightarrow O_2C(NO_2)_3 + KF + 1/2F_2 \qquad (26)$$

anions. There was no visible evidence of reaction when a mixture of O_2F_2 and $KC(NO_2)_3$ at -196°C was slowly warmed to room temperature. Gaseous impurities removed from the yellow solid residue from the reaction were: COF_2, SiF_4, N_2O, NO, NO_2, and various fluorocarbon compounds. Infrared analysis of the solid indicated it was a mixture of unreacted $KC(NO_2)_3$ and a fluosilicate.

2. Reactions of Trioxygen Difluoride

We have previously discussed the desirability of undertaking a study of the chemistry of O_3F_2 and described the manner in which we prepared a relatively pure samples of this material (Ref 9). Although it proved to be much more complicated to evaluate reactions with O_3F_2 than with O_2F_2, several exploratory reactions were carried out with the following reagents: Cl_2, AsF_5, NO, and $CsClF_4$. The results, in general, parallel those obtained with O_2F_2 except that in the reaction of Cl_2 with O_3F_2 (one run only) no intermediate purple addition product was observed.

a. Reaction of O_3F_2 with Cl_2

O_2F_2 reacts with chlorine to form a purple intermediate which reportedly has the composition $(O_2ClF_3)_n$ (Ref 10) and which decomposes above -78°C to yield O_2 and ClF_3. An analogous reaction was attempted with O_3F_2 at -160°C in an all-glass system. In this case there was no formation of purple adduct observed. The ultimate gaseous products formed (in addition to oxygen and fluorine) were ClO_2, ClO_2F, and ClO_3F.

b. Reaction of O_3F_2 with AsF_5

O_3F_2 was mixed with AsF_5 at -160°C and the mixture was allowed to remain at that temperature for 1.5 hours. Upon warming to room temperature, non-condensable decomposition gases and a white solid were present in the reactor. X-ray analysis showed the solid to be O_2AsF_6. The reaction probably occurred as shown in equation 27.

$$O_3F_2 + AsF_5 \longrightarrow O_2F_2 + AsF_5 + 1/2O_2 \longrightarrow O_2AsF_6 + 1/2O_2 + 1/2F_2 \qquad (27)$$

c. Reaction of O_3F_2 and NO

No volatile reaction products could be detected in a mixture of O_3F_2 and NO at -196°C or at -185°C. When the system was warmed to -78°C, NO_2 was formed.

d. Attempted Reaction of O_3F_2 with $NONF_2$

An attempt was made to study possible free radical coupling between paramagnetic O_3F_2 and the unstable adduct of NO with N_2F_4. Unfortunately, just as the purple $NONF_2$ adduct had been condensed onto O_3F_2 at -196°C, the reactor cracked and the experiment had to be abandoned. Further study of this system will be carried out at a later date.

e. Attempted Reaction of O_3F_2 with $CsClF_4$

As in the case of the attempted reaction of O_2F_2 with $CsClF_4$, RMD hoped that O_3F_2 would fluorinate the ClF_4^- anion. After treatment of $CsClF_4$ with O_3F_2 at -107°C for several hours, the system was raised to room temperature and a sample of the residual solid was subjected to x-ray analysis. The diffraction pattern indicated the presence of unreacted $CsClF_4$ and Cs_2SiF_6.

D. EXPERIMENTAL

Experimental details are given in this section only for those experiments performed during the last quarter of the program.

1. Reactions of O_2AsF_6

a. Reaction of O_2AsF_6 with NO_2ClO_4

The reaction of O_2AsF_6 with NO_2ClO_4 was carried out in a Pyrex round bottom flask having a "solids addition" side arm. Equimolar quantities of the two reagents were weighed in a dry atmosphere. One reagent was loaded into the flask along with a Teflon-coated magnetic stirring bar and the other reagent was loaded into the side arm. The flask was then attached to a vacuum system and evacuated. The side arm was rotated to allow the two reagents to mix at the desired reaction temperature (-78°C, 0°C, or ambient) and the solid mixture was stirred for several hours by means of the magnetic stirrer.

In two runs at -78°C (Table I, Section C), C_3F_8 was used as a reaction medium. After several hours of stirring the suspension, in the runs using C_3F_8, the flask was cooled to -196°C and the vapor pressure obtained. In both cases, this proved to be negligibly small. The solids were observed to remain white at -196°C and -78°C, but inconsistent results were observed after the C_3F_8 had been removed by pumping at room temperature. In Run No. 2 (Table I, Section C), no color change was observed at room temperature, but in Run No. 4 (Table I, Section C) the solid slowly turned yellow at room temperature and the color deepened on further handling of the solid to prepare x-ray samples.

The other runs (No. 1, 3, 5, and 6 — Table I) were conducted without the use of C_3F_8 and in each case the final solid was yellow. In these runs vapor pressures were observed at room temperature and samples of the vapors were analyzed by infrared and mass spectroscopy. In all cases some oxygen and ClO_3F (or Cl_2O_7) were observed in the vapor phase, but the total pressure was significantly less than the oxygen content of the initial dioxygenyl hexafluoroarsenate.

Samples were then prepared for x-ray analysis in a dry atmosphere box. There was no way of determining whether further gassing occurred during this procedure and while the x-ray patterns were photographed. In some instances, however, the samples deepened in color during the filling of x-ray capillaries. The x-ray patterns obtained were compared to known patterns for NO_2ClO_4, $NOClO_4$, NO_2AsF_6, $NOAsF_6$ (O_2AsF_6) (Figure 1, Section C).

b. Reaction of O_2AsF_6 with $KClO_4$ in IF_5

O_2AsF_6 was found to dissolve in redistilled IF_5 to give a stable solution at room temperature. The solid recovered from the solution exhibited an x-ray pattern identical to that previously reported (Ref 2) for O_2AsF_6.

To a solution of 0.27 mmole $KClO_4$ in three ml IF_5 was added 0.27 mmole O_2AsF_6. An orange oil appeared on the surface of the IF_5 but on further mixing the entire liquid phase became orange. The solution slowly evolved gas which was identified as a mixture of oxygen and ClO_3F. Upon removal of the IF_5 in vacuo a white solid was isolated. Its x-ray pattern was almost identical to a standard pattern of $KAsF_6$.

c. Reaction of Anhydrous $HClO_4$ with O_2AsF_6

In this experiment, anhydrous $HClO_4$, generated by distilling 70 percent $HClO_4$ from P_2O_5, was added to a small sample of O_2AsF_6 at -196°C. As the mixture was allowed to warm to room temperature, there was a vigorous evolution of gas, and the solution became yellow-green in color. The $HClO_4$ was distilled off in vacuo leaving only a trace of solid residue.

d. Reactions of Dichlorine Heptoxide

(1) Reaction of O_2AsF_6 with Cl_2O_7

A 0.3893 gram sample of O_2AsF_6 (1.76 mmoles) was loaded into a Kel-F reactor. A 1.0 cc quantity of 70 percent $HClO_4$ (2.83 fold stoichiometric excess over O_2AsF_6) was added in a vacuum to powdered P_2O_5, and the Cl_2O_7 so formed was transferred in a vacuum to the reactor held at -196°C. The reactor was then brought to -78°C and held at this temperature overnight. Mass spectral analysis of gases in the reactor after 16 hours showed the presence of the following constituents: ClO_3F, ClO_2F, O_2, and Cl_2. The solid residue was stored for five days at -78°C, and then evacuated at this temperature through a -196°C trap. The 0.117 mmole sample of gas removed in this way was ClO_3F. When the solid was allowed to warm to room temperature, it was speckled with grayish spots. The small amount of gas that came off of it at room temperature was SiF_4. A 0.0480 gm sample of the solid was hydrolyzed in a vacuum, but no gases were evolved as a result of this treatment. There was some insoluble material present in solution, which did not dissolve even when concentrated nitric acid was added. X-ray analysis of the original solid product showed the pattern of O_2AsF_6 or $NOAsF_6$. The two are indistinguishable by x-ray analysis.

(2) Reaction of O_2AsF_6 with $\cdot NF_2$ Radicals

Several experiments were run in attempting to effect a coupling of $\cdot NF_2$ with O_2^+. The procedure was used in these experiments was not varied significantly. The only major difference in the results from run to run was that the amount of N_2F_4 taken up by the solid O_2AsF_6 varied from 85 percent of theory for a 1:1 coupling of $\cdot NF_2$ with O_2^+ to an almost negligible uptake.

Difluoramino radicals were produced by passing N_2F_4 through an evacuated Monel tube at 250°C. The effluent gas stream was condensed on samples of O_2AsF_6 at -196°C. A description of a typical experiment follows:

A sample of O_2AsF_6 (1.42 mmoles) of O_2AsF_6 was treated at -196°C with 1.47 mmoles of pyrolyzed N_2F_4. Of this quantity of N_2F_4 0.107 mmole passed through the trap containing the O_2AsF_6 and was recovered in a second -196°C trap downstream. The mixture of adsorbed N_2F_4 (presumably as $\cdot NF_2$ radicals) and O_2AsF_6 were held at -90°C for two hours. A sample of gas condensable at -196°C removed from the reactor at this temperature consisted of N_2F_4, NO, N_2O, and CO_2. The reactor was then warmed to -78°C, at which temperature only a trace of gas was evolved. No gas was liberated from the solid upon warming to room temperature. The x-ray pattern of the residual solid indicated the presence of NO_2AsF_6 and $NOAsF_6$ or O_2AsF_6.

2. Reaction of O_2F_2 with $ClO\cdot AsF_5$

a. Preparation of $ClO\cdot AsF_5$

Cl_2O (approximately 1.25 mmoles) was prepared in $CFCl_3$ by reacting 2.5 mmoles Cl_2 with a slight excess of yellow HgO at 0°C for three hours in a 200 ml round bottom flask. The flask was wrapped with aluminum foil to exclude light. The Cl_2O and $CFCl_3$ were then distilled to a Kel-F trap at -196°C, which was connected on one side, through a low temperature vacuum valve, to a glass U-shaped discharge tube and on the other side to a vacuum manifold. At this point, 1.25 mmoles of AsF_5 was distilled on top of the frozen mixture of Cl_2O and $CFCl_3$ and the trap was isolated from the rest of the vacuum system and warmed to -78°C. A white solid was observed in the bottom of the tube and suspended in the liquid $CFCl_3$. This solid was presumably the $Cl_2O\cdot AsF_5$ adduct reported by Schmeisser (Ref 8). The suspension was warmed to -50°C and pumped until all of the $CFCl_3$ had been removed. The $CFCl_3$ condensed as a white solid downstream in a -196°C trap. A ring of yellow solid was observed in the trap. This was presumed to be chlorine ($Cl_2O\cdot AsF_5 \longrightarrow 1/2\,Cl_2 + ClO\cdot AsF_5$). After pumping the residual solid for one hour at -50°C, it was

recooled to -196°C and maintained at that temperature until the preparation and distillation of O_2F_2 was completed.

b. Reaction of $ClO \cdot AsF_5$ with O_2F_2

O_2F_2 was generated in the glass discharge tube at -196°C and distilled through a low temperature vacuum valve to the Kel-F trap containing $ClO \cdot AsF_5$. During this distillation, the loss of O_2F_2 was minimized as follows: (a) all connecting lines and the valve were cooled by packing with Dry Ice, (b) once the O_2F_2 preparation had been completed at -196°C, the liquid N_2 was poured out of the Dewar surrounding the discharge tube and the cold, empty Dewar was replaced under the discharge trap, and (c) the entire system was continuously pumped as the O_2F_2 melted and distilled into the Kel-F trap at -196°C.

The trap was again isolated from the vacuum system and warmed to -160°C, where the O_2F_2 melted and flowed onto the solid $ClO \cdot AsF_5$. A purple color appeared on the surface of the $ClO \cdot AsF_5$ on contact with O_2AsF_6. The solid was treated with three separate batches of O_2F_2 in order to insure complete reaction. The trap was then cooled to -196°C and evacuated to remove oxygen and fluorine. On warming to room temperature, approximately 50 mm of vapor pressure was observed above a solid and some liquid droplets. Mass spectral analysis of the vapors indicated the presence of ClO_3F, Cl_2, and traces of fluorocarbons.

After standing for one week the solid residue disappeared but the liquid droplets remained.

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SECTION IV

Task 54

STABILIZATION OF NITRONIUM PERCHLORATE

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Report RMD 5043-64-F

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FOREWORD

This section of the Advanced Oxidizer Final Report summarizes work conducted during the period from 1 January 1964 to 30 September 1964 on synthetic efforts directed toward the stabilization of nitronium perchlorate under Navy Contract NOnr4364(00), ARPA Order No. 417. During the third quarter of this program, efforts to stabilize nitronium perchlorate by chemical modification were terminated and personnel previously assigned to this task transferred their efforts to the study of difluorodiazine chemistry (Task 56).

Contributors to this study were: A. R. Young, II (Project Supervisor), J. Dvorak (Principal Investigator), B. Fagan (X-Ray Analysis), and J. Creatura (Wet Chemical Analysis).

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I. INTRODUCTION

The objective of this program was to increase the stability of nitronium perchlorate by chemical methods as opposed to physical coating techniques.

Reaction Motors Division's approach to achieving this objective consisted of attempts to prepare nitronium ion complexes of composition of NO_2-(ligand)$^+ClO_4^-$. Although specific impulse calculations indicate that the most desirable ligand molecules would be ammonia and hydrazine, preliminary studies revealed that the direct combination of nitronium perchlorate with ammonia or hydrazine was not feasible (Ref 1). It was believed, however, that complexes of nitronium perchlorate with less reactive ligands might serve as intermediates in the synthesis of ammonia or hydrazine complexes by ligand displacement reactions. Of the various potential ligands examined (Ref 1), only pyridine gave evidence of yielding an isolable complex. Although the white solid complex, $NO_2(C_5H_5N)^+ClO_4^-$, can be stored indefinitely at -78°C, it slowly decomposes at room temperature yielding a brown tar which contains pyridinium perchlorate. Attempts to substitute ammonia for pyridine in a non-metal cation-pyridine perchlorate produced only ammonium perchlorate.

It was concluded, therefore, that the chemical stabilization of nitronium perchlorate by complexation is not feasible. The studies leading to this conclusion are discussed in the following paragraphs.

II. DISCUSSION

During the period covered by this report considerable efforts were expended to incorporate energetic ligands directly in the NO_2ClO_4 molecule (Ref 1). The major effort during this period was directed toward the preparation of a pyridine complex of the nitronium ion which might subsequently be exchanged for a more energetic ligand.

A. ATTEMPTS TO PREPARE CATIONIC COMPLEXES OF NITRONIUM PERCHLORATE

1. Reaction of NO_2ClO_4 with Pyridine

Pyridine forms numerous complexes with metallic and non-metallic perchlorates (Ref 2, 3 and 4). In addition, complex salts such as $I(py)_2ClO_4$ and $Cl(py)NO_3$ are less hygroscopic and more thermally stable than the respective uncomplexed "salts". Therefore, it was decided to explore the possibility of preparing a pyridine complex of the nitronium ion, using nitronium perchlorate as a source of that ion. If the desired pyridine complex was obtained, it might serve as an intermediate for the preparation of more energetic complexes of nitronium perchlorate using ligands such as ammonia and hydrazine. This approach to energetic nitronium perchlorate complexes is shown in equations 1 and 2.

$$NO_2ClO_4 + C_5H_5N \longrightarrow NO_2(C_5H_5N)ClO_4 \qquad (1)$$

$$NO_2(C_5H_5N)ClO_4 + N_2H_4 \longrightarrow NO_2(N_2H_4)ClO_4 + C_5H_5N \qquad (2)$$

In an initial attempt to prepare a complex, pyridine was added to an acetonitrile solution containing an equimolar amount of NO_2ClO_4. The reaction mixture yielded an orange solid after removal of the acetonitrile in vacuo. The infrared spectrum of the solid showed absorptions attributable to ClO_4^- and NO_3^-, as well as aromatic ring vibrations indicative of a pyridinium ($C_5H_5NH^+$) salt. Analysis indicated the reaction product to be chemically non-homogeneous.

Similar results were obtained when NO_2ClO_4 was allowed to react with a large excess of pyridine in the absence of a solvent. The infrared spectrum of the solid product revealed absorptions attributable to ClO_4^- and the pyridinium ion. The amount of pyridinium ion present was too great to attribute to the presence of traces of moisture in the pyridine. It was concluded that pyridine provides the proton necessary to form $C_5H_5NH^+$. A possible reaction of NO_2ClO_4 with pyridine which would lead to the formation of pyridinium salts is shown in equation 3.

$$NO_2ClO_4 + C_5H_5N \longrightarrow O_2NC_5H_4N + HClO_4 \xrightarrow{C_5H_5N} \begin{cases} O_2NC_5H_4NHClO_4 \\ C_5H_5NHClO_4 \end{cases} \quad (3)$$

Different results were obtained when Freon-113 was used as the reaction medium. In several runs, summarized in Table I, products were obtained which consistently gave x-ray patterns almost identical to that of pure NO_2ClO_4, but which showed strong absorptions attributable to pyridine in the infrared. In each case the white solid product was storable at -78°C, but was slowly converted to a brown tar when standing at room temperature. The brown tar contained pyridinium perchlorate ($C_5H_5NH^+ClO_4^-$). Although analytical data were inconclusive, it is believed, on the basis of infrared spectra and because of the presence of pyridinium perchlorate in the decomposition products, that the solid obtained in the pyridine-nitronium perchlorate reaction in Freon is a pyridine complex, $NO_2(C_5H_5N)_x^+ClO_4^-$. The mode of decomposition of the complex is most probably as shown in equation 4.

$$C_5H_5N + NO_2ClO_4 \xrightarrow[-30^\circ C]{\text{Freon-113}} NO_2(C_5H_5N)^+ClO_4 \xrightarrow{\text{ambient}} O_2NC_5H_4N + H^+ + ClO_4^- \quad (4)$$

2. Reaction of $Ag(C_5H_5N)_2ClO_4$ with NO_2Cl

A possible alternate method for preparing a pyridine complex of NO_2ClO_4 is by a reaction of NO_2Cl with $Ag(C_5H_5N)_2ClO_4$. The feasibility of this approach was tested initially with commercially-available NOCl (equation 5) instead of NO_2Cl. When NOCl was added to nitromethane solution of $AgClO_4$ and pyridine,

$$Ag(C_5H_5N)_2ClO_4 + NOCl \longrightarrow AgCl + NO(C_5H_5N)_2ClO_4 \quad (5)$$

TABLE I

REACTIONS OF NO_2ClO_4 WITH PYRIDINE

Conditions			Results				
Mole Ratio NO_2ClO_4:Pyridine	Solvent	Reaction Temp (°C)	Type of Product	Product X-ray Pattern	IR Spectrum	Chemical Analysis	Ref
1:1	CH_3CN	Ambient	Yellow solid	--	Showed NO_3^-, ClO_4^-, and $C_5H_5NH^+$	Indicates non-homogeneous product	5
Excess pyridine	--	-20	Yellow - brown solid	Not previously encountered	Showed ClO_4^- and $C_5H_5NH^+$	--	6
1:1	Freon-113	-30	White solid decomposes at ambient temperature	Similar to NO_2ClO_4	Showed ClO_4^- and pyridine	Decomposed before analysis	5
1:1	Freon-113	-30	White solid, storable at -78°C	Similar to NO_2ClO_4	Showed NO_2^+, ClO_4^-, and pyridine	Decomposed before analysis	5
1:3	Freon-113	-30	White solid, storable at -78°C	Similar to NO_2ClO_4	Showed ClO_4^- and $C_5H_5NH^+$	Consistent with monopyridine complex of 80% purity	6

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AgCl precipitated as predicted by equation 5, but nitric oxide was simultaneously liberated. Removal of the solvent in vacuo yielded a solid product having an x-ray pattern similar to that obtained for the product of the reaction of NO_2ClO_4 with excess pyridine (Ref 7), which indicated that the product contained pyridinium salts. The infrared spectrum showed absorptions attributable to NO_3^-, ClO_4^-, and $C_5H_5NH^+$. Chemical analysis also indicated that the product was a mixture of $C_5H_5NHNO_3$ and $C_5H_5NHClO_4$.

When NOCl was added to a chloroform solution of $AgClO_4$ and pyridine, AgCl precipitated without evolution of nitric oxide. After the AgCl was separated by filtration, the filtrate was evaporated in vacuo. The residual solid contained 1.63 percent NO^+ which was considerably less than the theoretical 10.43 percent. Infrared and x-ray analysis indicated that the product was predominantly pyridinium perchlorate.

In a similar reaction, NOCl was added to a chloroform solution of $Ag(C_5H_5N)_2ClO_4$ and the precipitated AgCl was separated by filtration. The filtrate was added to an equal volume of ether, producing a white precipitate. The infrared spectrum and chemical analysis of this material were consistent with a mixture of pyridinium salts containing predominantly $C_5H_5NHNO_3$.

3. Reaction of $I(C_5H_5N)_2ClO_4$ with NO_2

An investigation of the preparation and chemical reactivity of dipyridine iodinium perchlorate, $I(C_5H_5N)_2ClO_4$, was undertaken as an alternate synthetic route to a pyridine complex of NO_2ClO_4. Examples of possible reactions leading to the desired complex nitronium perchlorate are given in equations 6, 7, 8 and 9.

$$Ag(C_5H_5N)_2ClO_4 + I_2 \longrightarrow I(C_5H_5N)_2ClO_4 + AgI \qquad (6)$$

$$2\,I(C_5H_5N)_2ClO_4 + N_2O_4 \xrightarrow{?} 2NO_2(C_5H_5N)_2ClO_4 + I_2 \qquad (7)$$

$$I(C_5H_5N)_2ClO_4 + NO_2Cl \xrightarrow{?} NO_2(C_5H_5N)_2ClO_4 + ICl \qquad (8)$$

$$I(C_5H_5N)_2ClO_4 + NO_2Cl \xrightarrow{?} NO_2(C_5H_5N)ClO_4 + ICl\cdot C_5H_5N \qquad (9)$$

$I(C_5H_5N)_2ClO_4$ is best prepared by adding iodine to a chloroform solution of $Ag(C_5H_5N)_2ClO_4$. The AgI which precipitates is separated by filtration and the filtrate, a chloroform solution of $I(C_5H_5N)_2ClO_4$, can be used for subsequent reactions. If desired, the solid $I(C_5H_5N)_2ClO_4$ can be isolated by adding the filtrate to an equal volume of ether and drying the resultant precipitate.

When NO_2 was added to a chloroform solution of $I(C_5H_5N)_2ClO_4$, a solid precipitated and the solution became intensely violent, indicating that iodine had been liberated. Analysis indicated, however, that the solid consisted of a mixture of pyridinium perchlorate and nitrate.

4. Reaction of $I(C_5H_5N)_2ClO_4$ with NH_3

The reaction of $I(C_5H_5N)_2ClO_4$ with NH_3 was investigated in an attempt to determine whether pyridine could be displaced from the complex salt (equation 10). The addition of NH_3 to a $CHCl_3$ solution of $I(C_5H_5N)_2ClO_4$ was found to result in the precipitation of NH_4ClO_4 and the liberation of iodine and pyridine.

$$I(C_5H_5N)_2ClO_4 + 2NH_3 \xrightarrow{?} I(NH_3)_2ClO_4 + 2C_5H_5N \qquad (10)$$

5. Reaction of NO_2ClO_4 with PF_3 and with PCl_3

To determine whether a phosphorous donor might complex with NO_2ClO_4, reactions of PF_3 and of PCl_3 with NO_2ClO_4 were investigated. No reaction occurred between NO_2ClO_4 and PF_3, but, PCl_3 was found to react with NO_2ClO_4 to yield $NOClO_4$ and $POCl_3$ (equation 11). The solid product was characterized

$$NO_2ClO_4 \text{ and } POCl_3 \longrightarrow NOClO_4 + POCl_3 \qquad (11)$$

by its x-ray diffraction pattern; the volatile reaction product was identified as $POCl_3$ by its mass spectrum.

6. Reaction of NO_2ClO_4 with N_2H_5Cl

An attempt to prepare a nitrosylhydrazinium cation ($NON_2H_5^+$) as shown in equation 12, resulted instead in the double displacement reaction shown in equation 13 (Ref 1).

$$NOClO_4 + N_2H_5Cl \xrightarrow{NOCl} NON_2H_5(ClO_4)Cl \qquad (12)$$

$$NOClO_4 + N_2H_5Cl \xrightarrow{NOCl} NOCl + N_2H_5ClO_4 \qquad (13)$$

Therefore, an attempt was made to prepare nitrylhydrazinium perchlorate $[NO_2N_2H_5(ClO_4)]$ by reacting N_2H_5Cl with excess NO_2ClO_4 (equations 14 and 15).

$$NO_2ClO_4 + N_2H_5Cl \xrightarrow{?} N_2H_5ClO_4 + NO_2Cl \qquad (14)$$

$$NO_2ClO_4 + N_2H_5ClO_4 \xrightarrow{?} NO_2N_2H_5(ClO_4)_2 \qquad (15)$$

When NO_2ClO_4 was mixed with N_2H_5Cl in the solid state, a violent reaction occurred. Noncondensable gases, as well as Cl_2, NO_2, and N_2O were generated. A less vigorous decomposition occurred when the reaction was conducted in nitromethane. Nitrogen, nitrogen oxides, chlorine, chlorine oxides, and HCl were identified as gaseous decomposition products. No solid residue was present upon removal of the solvent.

B. ATTEMPTS TO PREPARE OTHER ENERGETIC PERCHLORATES

1. Reaction of Nitronium Perchlorate with Perchlorate Acid

The reaction of NO_2ClO_4 with anhydrous $HClO_4$ was investigated in an effort to obtain a stable complex perchlorate (equation 16). Anhydrous perchloric

$$NO_2ClO_4 + xHClO_4 \xrightarrow{?} NO_2ClO_4 \cdot xHClO_4 \qquad (16)$$

acid was condensed on NO_2ClO_4 at -196°C, and the mixture was allowed to warm to room temperature. After stirring the resultant solution for several hours, the perchloric acid was removed *in vacuo*. The residual white solid had an x-ray powder pattern (Table II) similar to that reported for the so called nitronium perchlorate-hydrate (Ref 8). The infrared spectrum of the reaction product, obtained as a mull, showed absorptions attributable to OH, NO_2^+, and ClO_4^-. Chemical analysis, however, was in excellent agreement with theory for pure NO_2ClO_4 (Table III).

TABLE II

X-RAY DIFFRACTION PATTERN OF RESIDUE FROM NO_2ClO_4-$HClO_4$ SOLUTION

d	I/Io
14.98	30
9.51	5
8.08	7
7.78	3
6.78	4
5.12	10
5.45	12
5.16	30
4.74	25
4.53	40
4.25	10
4.05	12
3.88	5
3.76	7
3.49	12
3.36	2
3.27	15
3.16	100
3.09	30
2.94	40
2.34	15

TABLE III

ANALYSIS OF NO_2ClO_4-$HClO_4$ REACTION PRODUCT

Element or Group	Found (%)	Calcd. for NO_2ClO_4 (%)
N	9.76	9.62
ClO_4^-	68.19	68.38

It is possible that a monohydrate of NO_2ClO_4 could have formed through a sequence of reactions such as shown below in equations 17 and 18:

$$2HClO_4 \longrightarrow Cl_2O_7 + H_2O \qquad (17)$$

$$NO_2ClO_4 + H_2O \longrightarrow NO_2ClO_4 \cdot H_2O \qquad (18)$$

However, chemical analysis indicates the residue from the NO_2ClO_4 - $HClO_4$ solution is predominantly pure NO_2ClO_4. It therefore appears that no reaction took place. An explanation for the x-ray pattern is not immediately apparent.

2. Reaction of NH_3OHClO_4 with Perchloric Acid

The reaction of NH_3OHClO_4 with perchloric acid was pursued in an attempt to prepare a new perchloric acid adduct (equation 19). Excess anhydrous

$$NH_3OHClO_4 + xHClO_4 \xrightarrow{?} NH_3OHClO_4 \cdot xHClO_4 \qquad (19)$$

perchloric acid was condensed on $H_3NOHClO_4$ at -196°C. The reaction mixture was allowed to warm to room temperature with stirring. After removal of the $HClO_4$ in vacuo from the resultant solution, the NH_3OHClO_4 was recovered unchanged as shown by perchlorate analysis.

3. Reaction of NH_3OHClO_4 with ClO_3F

The reaction of NH_3OHClO_4 with ClO_3F was investigated in an attempt to prepare a perchloratoammonium salt, $NH_3ClO_4^+ClO_4^-$ (equation 20). In an

$$NH_3OHClO_4 + ClO_3F \xrightarrow{?} NH_3ClO_4^+ClO_4^- + HF \qquad (20)$$

initial experiment, ClO_3F was added to an aqueous solution of NH_3OHClO_4. After stirring the reaction mixture for several hours, the ClO_3F was recovered and the water was evaporated *in vacuo*. The residual white solid was identified by its infrared spectrum and x-ray pattern as NH_3OHClO_4. In a second experiment, ClO_3F was added to anhydrous NH_3OHClO_4. No reaction occurred, however, even after heating the reactants for several hours at 50°C.

Since ammonolysis of ClO_3F in liquid ammonia is greatly accelerated by base catalysis (Ref 9), a third reaction between ClO_3F and NH_3OHClO_4 was conducted in dioxane, an excellent solvent for ClO_3F. After stirring the reaction mixture at ambient temperatures for 12 hours, a slight pressure drop was observed. Analysis of the gaseous fraction showed that it contained predominantly ClO_3F, with lesser amounts of N_2O and CO_2. Evaporation of the dioxane *in vacuo* yielded a pale yellow solid. The infrared spectrum of the solid, obtained as a mull, had absorptions attributable to NH_3OHClO_4.

III. EXPERIMENTAL

Experimental details not reported below have been described in previous reports (Ref 5 and 6).

A. REACTION OF NO_2ClO_4 AND $HClO_4$

Anhydrous $HClO_4$ was prepared by dehydrating 70 percent $HClO_4$ with the requisite amount of fuming H_2SO_4 (Ref 10). The $HClO_4$ generated was collected at -78°C and then transferred to a trap containing NO_2ClO_4 cooled to -196°C. For example, approximately 1.5 cc of anhydrous $HClO_4$ was condensed on 0.34 gm of NO_2ClO_4 at -196°C. The reaction mixture was allowed to warm to room temperature with stirring. Subsequently, the excess $HClO_4$ was removed in vacuo. The x-ray powder pattern of the residual solid is given in Table II and the chemical analysis in Table III.

B. REACTION OF NH_3OHClO_4 AND $HClO_4$

To 0.267 gm (two mmoles) of NH_3OHClO_4 at -196°C was added approximately 2 cc of anhydrous $HClO_4$. The reaction mixture was allowed to warm to room temperature. After stirring for 15 minutes at ambient temperatures, the $HClO_4$ was slowly removed in vacuo. The NH_3OHClO_4 was found to be unchanged on the basis of x-ray analysis.

C. REACTION OF NH_3OHClO_4 WITH ClO_3F

The NH_3OHClO_4 was prepared by the reaction of $Ba(ClO_4)_2$ with NH_3OHCl according to the method described by Robson (Ref 11).

1. Aqueous Solution

To a solution of 0.4846 gm (3.63 mmole) of NH_3OHClO_4 in five ml of water at -196°C was added 4.5 mmoles of ClO_3F. The reaction mixture was then allowed to warm to room temperature. No change in pressure was observed even after stirring the mixture for several hours. The ClO_3F was recovered and the unreacted NH_3OHClO_4 was isolated by pumping on the aqueous solution at 50°C.

2. No Solvent

To 0.467gm (3.5 mmoles) of NH_3OHClO_4 was added 4.0 mmoles of ClO_3F. The reaction mixture was allowed to warm to room temperature and then heated at 50°C for several hours with stirring. Both the ClO_3F and NH_3OHClO_4 were recovered.

3. In Dioxane

To a solution of 0.5342 gm (4.0 mmoles) of NH_3OHClO_4 in 20 ml of dioxane cooled to -196°C was added four mmoles of ClO_3F. The reaction mixture was stirred at ambient temperatures for 12 hours. A slight pressure drop was observed. The gaseous fraction contained predominantly ClO_3F with lesser amounts of N_2O and CO_2. Evaporation of the solvent in vacuo yielded a pale yellow solid exhibiting an infrared spectrum with absorptions attributable to NH_3OHClO_4. An attempt to dry the solid further by pumping on it at 50°C resulted in decomposition of the entire mass.

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2. C. Schumacher (ed.), Perchlorates, Their Properties, Manufacture and Uses, p. 47, Reinhold Publishing Corporation (1960).

3. G. Brauer, Handbook of Preparative Inorganic Chemistry, Vol. 1, Academic Press (1963).

4. H. Carlsohn, German Patent Number 692,324 (1940).

5. Thiokol Chemical Corporation, Reaction Motors Division, Report RMD 5043-Q1-64, Advanced Oxidizer Research, March 1964.

6. Thiokol Chemical Corporation, Reaction Motors Division, Report RMD 5043-Q2-64, Advanced Oxidizer Research, June 1964.

7. Ibid.

8. Callery Chemical Corporation, QPR-7, Contract DA-31-124-ARO(D)-12, 23 December 1963 to 1 March 1964.

9. H. Mandell and G. Barth-Wehrenalp, J. Inorg. Nucl. Chem., 12, 40 (1959).

10. G. Frederick Smith, J. Am. Chem. Soc., 75, 184 (1953).

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CONFIDENTIAL

Thiokol
REACTION MOTORS DIVISION

SECTION V

THERMAL STABILITY OF ADVANCED SOLID OXIDIZERS

C. J. Grelecki
W. Cruice

Report RMD 5043-64-F

RMD Project 5043, Task 55
Report Period: 31 December 1964 to
1 January 1964

Contract No. NOnr 4364(00)
ARPA Order No. 417
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CONFIDENTIAL

FOREWORD

This section of the report summarizes the work carried out during the period from 1 January 1964 to 31 December 1964 on the thermal stability of advanced solid oxidizers (RMD Project 5043, Task 55).

Contributors to the research were: C. Grelecki (Project Supervisor) and W. Cruice (Principal Investigator).

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I. INTRODUCTION

A number of advanced solid oxidizers are in various stages of research or development and complete characterization of their properties is required before their role in solid propellants can be determined. One of the most important properties is the thermal stability of the oxidizer because this limits the storage life and operational temperature limits of the propellant. In addition, propellant combustion characteristics are often intimately related to the decomposition of the oxidizer.

High-energy oxidizers of current interest include hydrazinium diperchlorate, nitronium perchlorate, and hydroxylammonium perchlorate. From an overall point of view, including performance and handling, hydrazinium diperchlorate appears to be the most feasible new oxidizer. As an example, because of its increased energy and density, substitution of hydrazinium diperchlorate for ammonium perchlorate can increase the range of the current Minuteman missile by 70 percent. Nitronium perchlorate gives slightly higher performance under analogous conditions; however, the problems associated with its stability and handling are more severe. In general, the higher the energy the more unstable the oxidizer, and the future high energy oxidizers can be expected to be accompanied by thermal stability problems. An understanding of the mechanism by which oxidizers decompose is important in defining conditions under which they can be prepared and handled. In addition, such an understanding could conceivably result in modifications which may improve their properties.

Thiokol Chemical Corporation, Reaction Motors Division, has been conducting a quantitative study of the thermal decomposition of hydrazinium diperchlorate for more than a year before the beginning of RMD Project 5043, Task 55. Many of the features of its thermal decomposition have been defined, but a considerable amount of additional work is required to adequately describe its reaction mechanism.

The objective of Task 55 was to study the kinetics of the thermal decomposition reactions of high-energy solid oxidizers in order to obtain a thorough understanding of the mechanism by which they decompose. A thorough examination of the literature, correlation of existing information, and supplementary

laboratory work to render as complete an understanding as possible of the field have been the three primary approaches employed.

Although hydrazinium diperchlorate is the most likely candidate for use as an improvement over presently used oxidizers, the reaction is so complex that this study began with perchloric acid, hydrazinium monoperchlorate, and hydroxylammonium perchlorate, inasmuch as these compounds were expected to undergo more elementary processes, relatively speaking. The information obtained, on the acid and the monoperchlorate in particular, as well as the experimental techniques developed, could then be used as a firm base for elucidation of the decomposition mechanism for the diperchlorate.

A literature survey made at the beginning of the program is included in Appendix A.

Experimental work on anhydrous perchloric acid and hydrazinium monoperchlorate has been presented in the form of articles submitted for publication to the Journal of Physical Chemistry. Experimental work performed on hydroxylammonium perchlorate has been presented as Appendix B.

II. MANUSCRIPTS OF PAPERS FOR PUBLICATION

The Vapor Pressure of Anhydrous Perchloric Acid
and
The Thermal Decomposition of Hydrazinium Monoperchlorate

Prepared for Submission to
Journal of Physical Chemistry

Contribution from the Chemistry Department, Reaction Motors, Division, Thiokol Chemical Corporation, Denville, New Jersey

The Vapor Pressure of Anhydrous Perchloric Acid[1]

Chester J. Grelecki and William J. Cruice

(1) This work was supported by the Advanced Research Projects Agency and administered by the Department of the Navy, Office of Naval Research, under Contract NOnr 4364(00).

INTRODUCTION

Although a considerable number of studies have been performed on the thermal decomposition and properties of perchloric acid, both dilute and highly concentrated, only two vapor pressure points appear in the literature for the anhydrous form. Van Wyk[2] reported a vapor pressure of 18 mm Hg at 16°C

(2) H. J. Van Wyk, Z. anorg chem, 48, 1 (1906).

in 1906, and Vorlander and von Schilling[3] reported a vapor pressure of 56 mm Hg

(3) D. Vorlander and R. von Schilling, Ann Chem, 310, 369 (1900).

at 39°C in 1900. Application of the Clausius-Clapeyron equation between these two points yields a value of 8.71 kcal/mole for the heat of vaporization. Extrapolation to 760 mm Hg yields 109°C for the boiling point and 22.8 e.u./mole for the entropy of vaporization.

This work was performed to extend and confirm data on vapor pressures and thermal decomposition of the anhydrous acid and as the first step in a series of studies on ammoniacal salts such as hydrazinium perchlorate, hydroxylammonium perchlorate, and hydrazinium diperchlorate.

EXPERIMENTAL

Anhydrous perchloric acid was prepared according to the method of G. Frederick Smith.[4] Thirty milliliters of oleum was added to 10 ml of 72

(4) G. F. Smith, J. Am. Chem. Soc., 75, 184(1952).

percent $HClO_4$ in a flask at 0°C, the flask was connected through all-glass tubing to a collecting trap at -78°C, and the trap was then connected to a vacuum line at 0.05 mm Hg. The flask and contents were permitted to come to ambient temperature with constant stirring, and pure anhydrous $HClO_4$ was evolved at two to four cc/hr. When production was completed (~five cc) a sample was quickly removed in a Teflon syringe tube, dissolved in distilled water and weighed by difference. Purity was determined by titration with standard 0.1 N NaOH to the phenolphthalien end point. The lowest assay of any sample was 99.28 percent; more common assays ranged from 99.50 to 99.95 percent. All samples were spot tested for $SO_4^=$ with $BaCl_2$. Only samples which gave a negative $SO_4^=$ test were used for the vapor pressure studies.

Vapor pressure measurements were made in an all-glass constant-volume modified sickle gauge illustrated in Figure 1. About 0.5 cc of anhydrous $HClO_4$ was introduced into the sample chamber with a Teflon syringe tube. The gauge assembly was then evacuated on sample and reference sides of the diaphragm to a pressure of less than 0.1 mm Hg (the sample being held at -78°C) and the loading arm sealed with a torch. A zero reference was selected between the needle and wire, the cold bath was removed and a thermostated Nujol bath was raised such that the entire sample chamber was submerged. Temperature was accurately monitored with a prestandardized thermocouple in the well in the bottom of the sample chamber and read on an L and N "H" Azar recorder to an accuracy of ±0.5°C. The reference chamber was backpressured to restore the zero reference and the pressure read on a common mercury manometer once constant temperature in the sample chamber was established. Readings are repeated after a period of 30 to 45 minutes to ensure equilibrium.

The probability of some decomposition occurring at even ambient temperatures is such that only a few points may be taken on any one sample. Confining each run to a reasonably small range of temperatures provides satisfactory results.

Subsequently, to obtain better conditions and additional information, as well as confirmation of points already obtained, the gauge was held at constant temperature and pressure was measured as a function of time. Samples used in these experiments were exactly 0.5 cc each, so that comparative rate data at different temperatures could be obtained. Vapor pressures were obtained by extrapolation of the P versus t curve to t = 0.

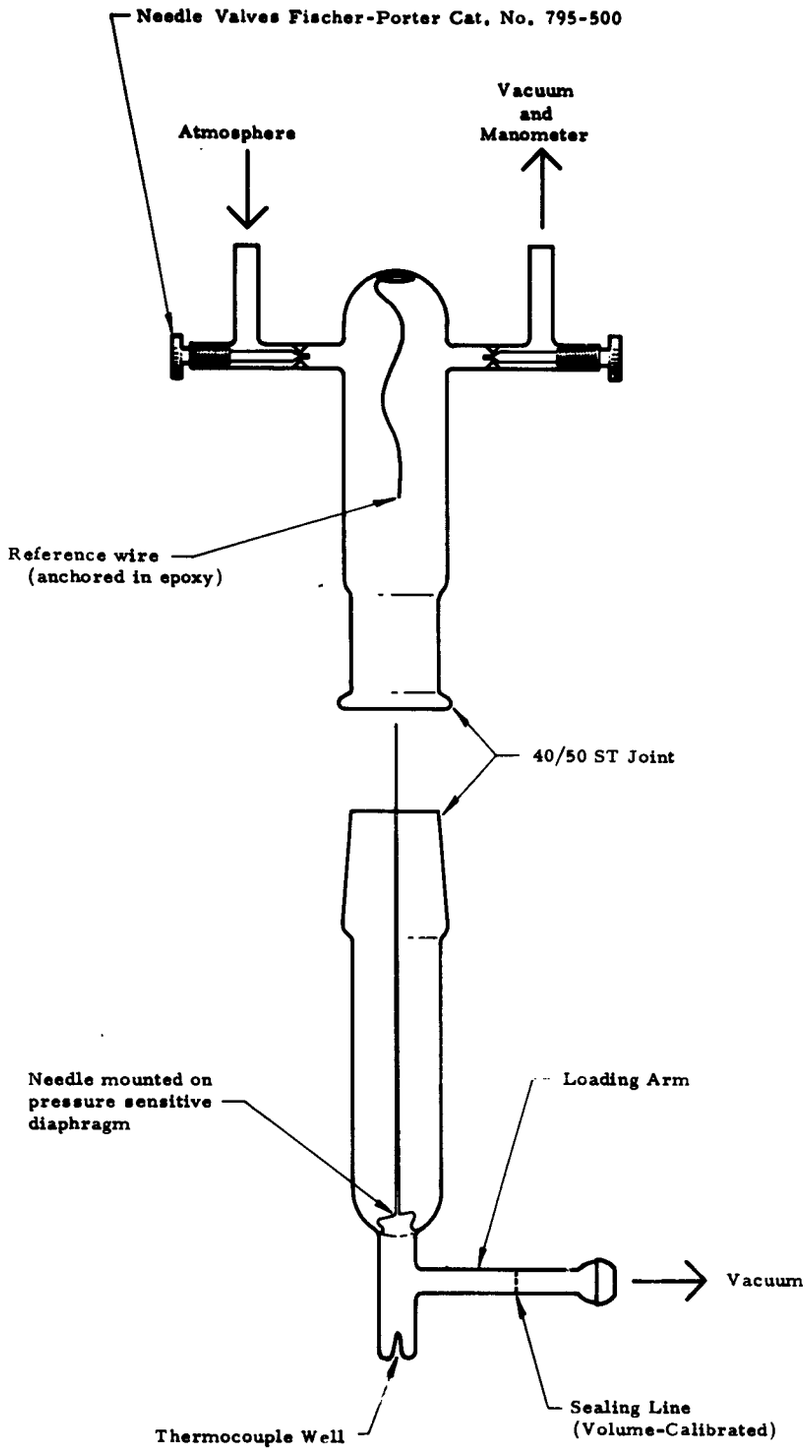

Figure 1. Sickle Gauge Apparatus

RESULTS AND DISCUSSION

Vapor Pressure of Anhydrous $HClO_4$

The results of several experiments are tabulated below:

T °C	16.6	20	25	29	35	40	41	46	51	61.5
P mm Hg	10	12	18	26	41	62	71	82*	102*	146**

*Sample slightly discolored; yellowish.
**Sample dark brown liquid [illegible]

The deviation of the latter three points from the expected straight line log P versus 1/T °K (see Figure 2) is presumed to be a result of [illegible] decomposition according to the equation

$$3\ HClO_4 \longrightarrow Cl_2O_7 + OH_3ClO_4$$

The presence of these compounds should substantially reduce the vapor pressure of the sample. Application of the Clausius-Clapeyron equation to the results yields a value of 15.03 kcal/mole for the heat of vaporization. Extrapolation to P = 760 mm Hg yields a predicted boiling point of 78°C and an extremely high entropy of vaporization of 42.82 e.u./mole. The value obtained from the curve for the vapor pressure at 39°C is in excellent agreement with the point reported by Vorlander and von Schilling; the point reported by Van Wyk was not reproducible.

Thermal Decomposition of Anhydrous $HClO_4$

Plots of P versus t for 0.5 cc of $HClO_4$ in sickle gauge sample chambers of exactly 12.5 cc are illustrated in Figure 3. The curves show the initial build-up of vapor to the equilibrium vapor pressure, the induction period during which the sample changes gradually from a colorless liquid through gradually deepening shades of yellow, orange, and red, and the final stage during which the sample is dark reddish brown and pressure rises at a greatly increased rate.

The activation energy for the overall reaction can be calculated from these curves on the assumption that the concentrations of all species are the same at corresponding points on the P versus t curve. The time to a fixed dP/dt point is then inversely proportional to the overall specific rate constant, k, and E_a may be calculated from:

$$\frac{t_1}{t_2} = \frac{E_a}{R}\left[\frac{T_2 - T_1}{T_2 T_1}\right]$$

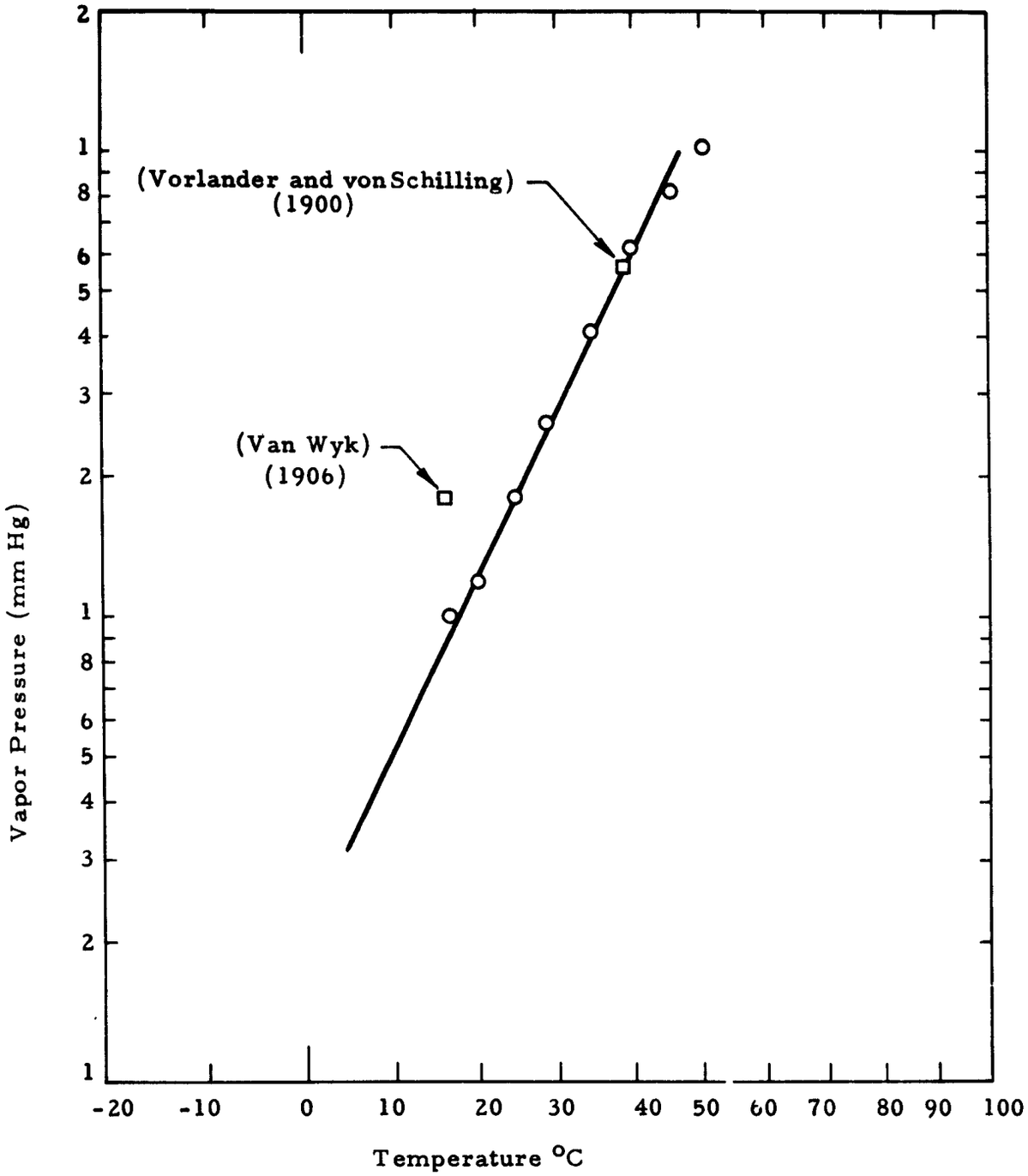

Figure 2. Vapor Pressure of Anhydrous Perchloric Acid

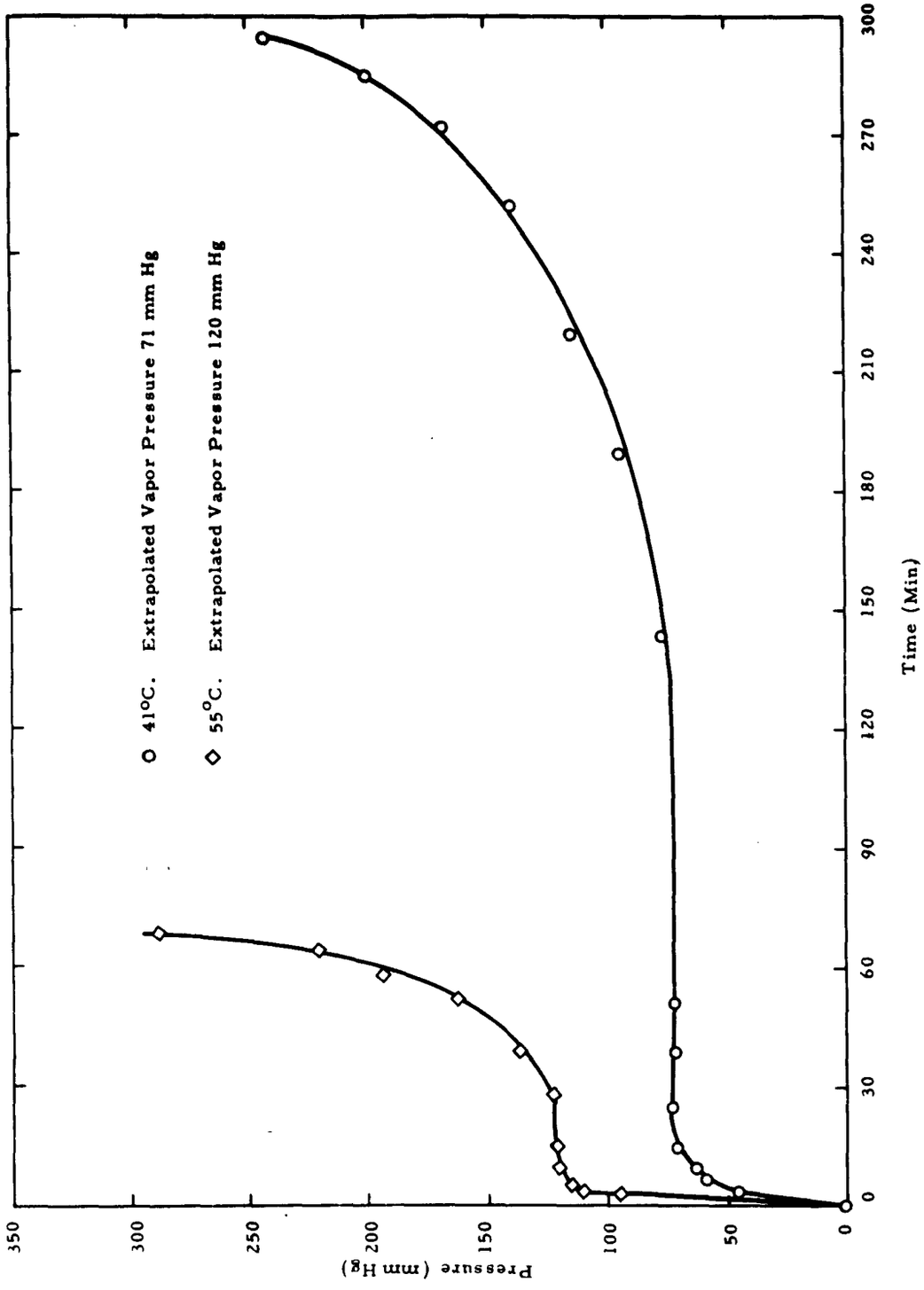

Figure 3. Pressure Versus Time Curves for Anhydrous $HClO_4$

Two sets of points were chosen as mutual checks. The first set is taken as the time at which the linear portion of the curve ends (i.e., the duration of the induction period); the second set is arbitrarily taken as the time at which P = 200 mm Hg. The results, tabulated below, are in excellent agreement with the values reported by Soviet investigators.[5, 6]

Source	41°C	55°C	E_a
Induction Period	129 min	28 min	22.4
t (P = 200 mm Hg)	285 min	59 min	23.1
Soviet Report No. 1 (5)	--	--	22.2
Soviet Report No. 2 (6)	--	--	22.6

(5) A. A. Zinov'ev and A. B. Tsentsiper, Zhur Neorg. Khim., 4, 724 (1959).

(6) A. B. Tsentsiper, Zhur. Neorg. Khim., 4, 1086 (1959).

It is presumed from the physical properties of the sample (color, most specifically) and the rapid rate of pressure increase that the reaction proceeds through the decomposition of Cl_2O_7 to Cl_2O_6 which rapidly decomposes to ClO_2 and O_2.

The value of the vapor pressure obtained by extrapolation of the curve at 41°C is 71 mm Hg, in good agreement with values obtained in previous vapor pressure runs. The value obtained from extrapolation of the curve at 55°C is 120 mm Hg, much lower than the expected value. The analysis of this sample, performed simultaneously with the decomposition run, gave a value of 104.6 percent purity, indicating super-dehydration of the dihydrate to give some Cl_2O_7 during production. The presence of Cl_2O_7, as previously stated, should lower the vapor pressure of the sample. This variance in initial concentration does not affect the calculation of E_a from kinetic data, however, a fact substantiated by the findings of several Soviet investigators.[6, 7]

(7) A. A. Zinov'ev and V. P. Babaeva, Zhur. Neorg. Khim., 6, 271 (1961).

A single experiment was performed on the decomposition of anhydrous $HClO_4$ in the vapor phase at 139°C. The initial pressure was 67 mm Hg; after almost 65 hr, the pressure had risen to 85 mm Hg. Assuming a first order stoichiometry following the expression:

$$HClO_4 \longrightarrow 1/2\ H_2O + 1/2\ Cl_2 + 1\text{-}3/4\ O_2$$

as proposed by Levy,[8] the first order rate constant has a value of 1.16×10^{-4}

(8) J. B. Levy, J. Phys. Chem., 66, 1092 (1962).

min^{-1}, approximately within the range expected by extrapolation of Levy's plot of k versus T°K. The scatter in data obtained at the lower temperatures in his experiments allows for a wide variation at 139°C, however, so that such "correlation" is interesting but insignificant.

Contribution from the Chemistry Department, Reaction Motors Division, Thiokol Chemical Corporation, Denville, N. J.

THE THERMAL DECOMPOSITION OF HYDRAZINIUM MONOPERCHLORATE[1]

Chester J. Grelecki and William J. Cruice

(1) This work was supported by the Advanced Research Projects Agency and administered by the Department of the Navy, Office of Naval Research, under Contract NOnr 4364(00).

INTRODUCTION

Hydrazinium monoperchlorate was first reported by Salvadori[2] in 1907.

(2) R. Salvadori, J. Soc. Chem. Ind, 26, 1066 (1908) (abstract: Gazz chim ital, 37, II, 32 (1907).

A number of papers has since appeared enumerating physical and chemical properties of this compound; however only slight mention is made of the quantitative examination of the thermal decomposition of the salt. Salvadori reported decomposition after prolonged heating in the range of 131 to 132°C, a rapid increase in reaction rate with increased temperatures, and explosion at 240°C. Barlot and Marsaule[3] report melting at 137 to 138°C and decomposition

(3) J. Barlot and S. Marsaule, Compt. Rend. Acad. des Sc., 228, 1497 (1949).

beginning at 145°C. The most recent information was reported by Shidlovskii, Semishin, and Shmagin,[4] who studied weight losses by 0.2 gm samples over a

(4) A. A. Schidlovskii, V. I. Semishin and C. F. Shmagin, Zh Priklad Khim, 35, (No. 4), 756 (1962).

six minute period at temperatures from 160°C to 250°C, the burning characteristics of the pure salt, and the effects of MnO_2, CoO, and Cu_2Cl_2 on both thermal decomposition and burning rate.

This work was performed to further elucidate the kinetic parameters, stoichiometry, and mechanism of decomposition of hydrazinium monoperchlorate as part of a general study of the thermal decomposition of ammoniacal salts of perchloric acid.

EXPERIMENTAL

Preparation

High purity hydrazinium monoperchlorate is conveniently prepared by neutralizing 60 percent $HClO_4$ with 75 percent N_2H_4 at temperatures from 0^oC to 25^oC. The salt precipitates from water at 0^oC and is filtered cold in scintered glass funnels. The fine white crystals are gently removed from the filter with a Teflon spatula and placed in a drying tube at 70^oC for two hours at constant vacuum of 0.05 mm Hg to break down the hemihydrate. Samples are titrated either potentiometrically or with phenolphthalien indicator by 0.1000 N NaOH. Characteristic purity factors range from 99.83 percent to 99.94 percent. As an additional estimate of purity, a DTA is run on each batch before use; a characteristic DTA is illustrated in Figure 1. The major endotherm at 137^oC to 150^oC (peak at 143^oC) represents melting; the major exotherm represents deflagration. Careful examination of the curve shows a small endotherm at 95^oC; this is an indication of the minuscular amount of water of hydration remaining in the sample.

Apparatus

Thermal decomposition runs are carried out in all-glass modified sickle gauges as illustrated in Figure 2. The apparatus consists of a pressure sensitive glass diaphragm, a spherical reactor, a glass seal-off arm for introduction of the sample and a glass break-seal for sampling decomposition products into the Bendix mass spectrometer. Sample sizes were varied from 0.090 to 0.342 gm; sample chambers from 12 to 28 ml and the diameter of the spherical reactor was varied from 2.5 to 3.0 cm. The entire assembly was pumped down to 0.005 mm Hg for 30 minutes at ambient temperature before seal-off. Runs were performed in thermostated baths of Dow Corning 500 Silicone oil controlled to $\pm 0.05^oC$ and checked by ASTM thermometers and an L and N Speedomax "H" Azar recorder. The gauge assembly acts as a null device and is sensitive to differences in pressure of 0.5 mm Hg between the reactor and the reference sides of the diaphragm. The reference side is backpressured to restore the null point and the pressure is measured with a mercury manometer.

RESULTS

Kinetic Data

Pressure versus time data were collected at temperatures from 130^oC to 200^oC. For convenience in comparing different systems, all data were

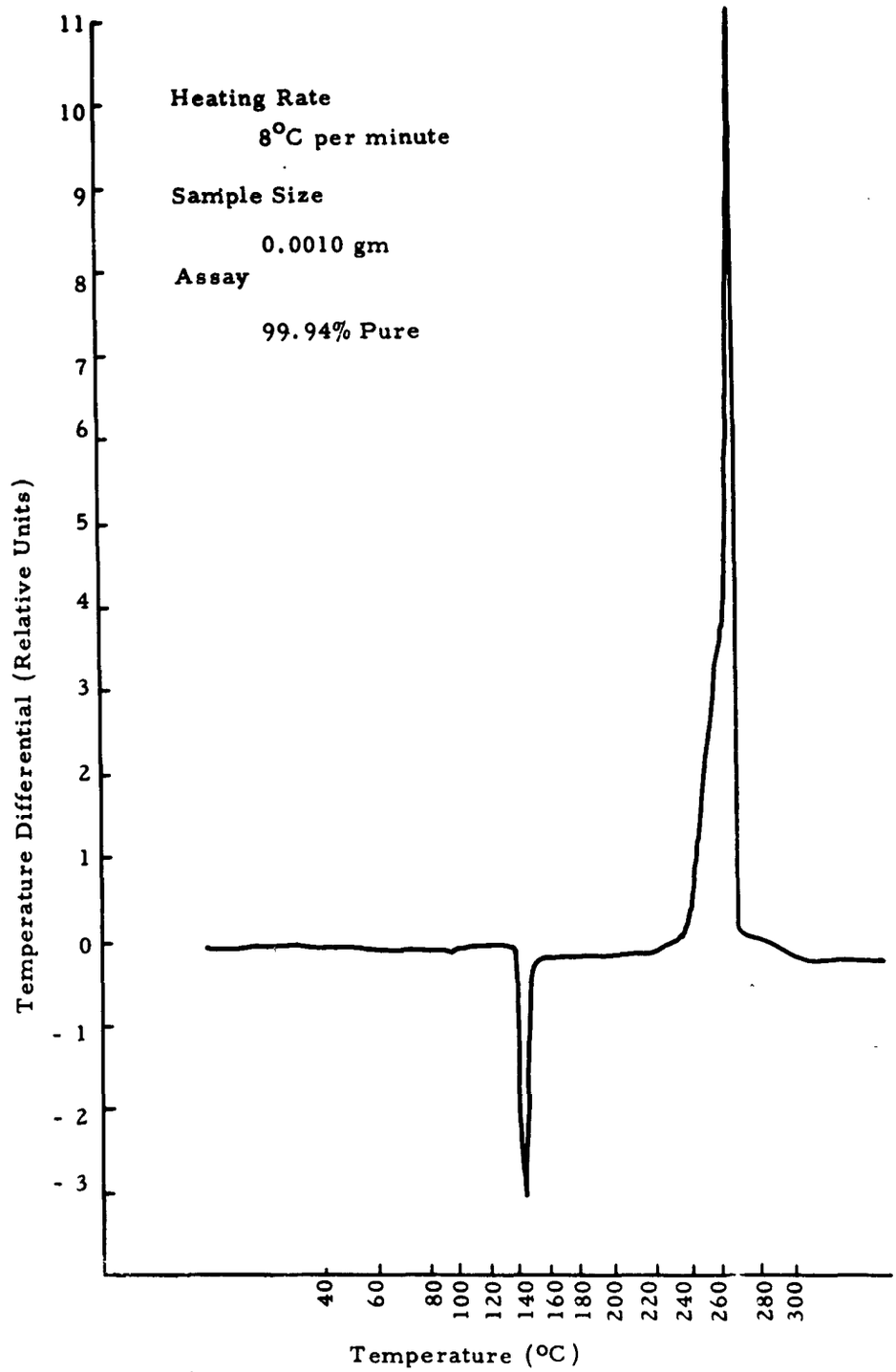

Figure 1. DTA Curve of High Purity Hydrazinium Perchlorate

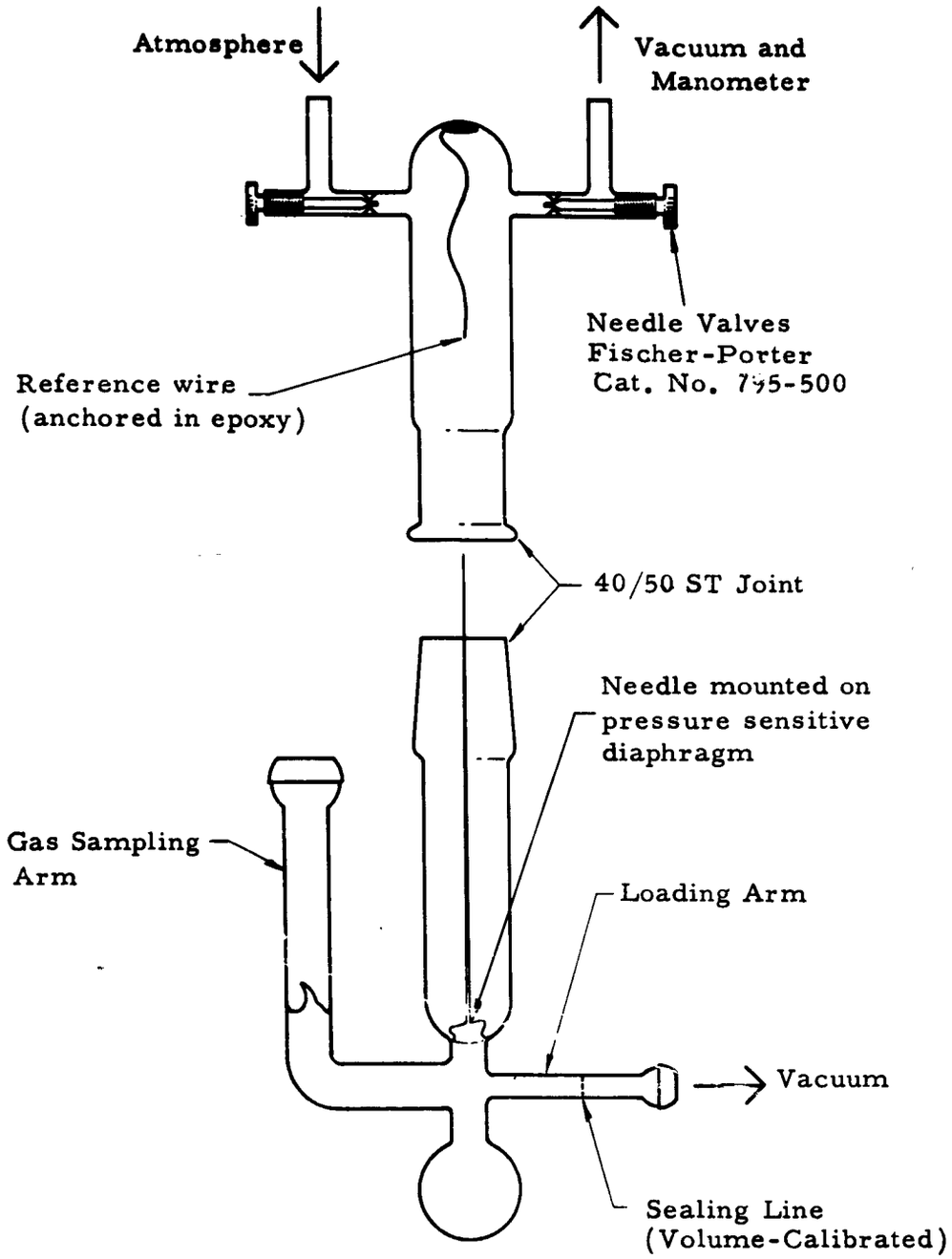

Figure 2. Stickle Gauge Apparatus

reducted to n/No versus time, where n = moles of gaseous product (PV/RT) and No = moles of hydrazine perchlorate initially present. Plots at various temperatures are contained in Figures 3 and 4. Over the range studied the reaction occurs in two distinct phases. The first stage follows the expression $n/No = At^2 + B$ quite well; the second stage follows a linear relationship :$n/No = C(t-D)$. Values of A, B, C, D, and also of ti and n/No at ti (where ti = time of transformation from power law to linear law) are tabulated below:

Temperature Coefficients of Decomposition of HP

T(°C)	A X 10^8	B	C X 10^4	D	ti*	n/No at ti*
140	6.25	0	1.31	552	1200	0.090
150	22.9	0	3.25	320	480	0.080
158	107	-0.006	6.9	166	300	0.090
170	260	-0.020	10.9	104	170	0.070
181	1070	0	21.0	53	95	0.090
200	18,000	-0.020	86.0	10	27	0.140

* Approximate values-time in minutes.

A plot of values of log C versus 1/T°K (Figure 5) gives an activation energy for the linear portion of the curve of 23.8 kcal/mole from 140°C to 200°C. No decomposition was observed for over 6000 minutes at 130°C.

Stoichiometry

Residual pressures at room temperature some time after the sickle gauge has been removed from the high temperature bath are converted to moles for comparison with the final reading at elevated temperature. At lower reaction temperatures (140°C to 158°C) the molar ratio of uncondensed gases to condensed gases is characteristically unity. At higher reaction temperatures this value decreases to 0.85 at 181°C and 0.79 at 190°C.

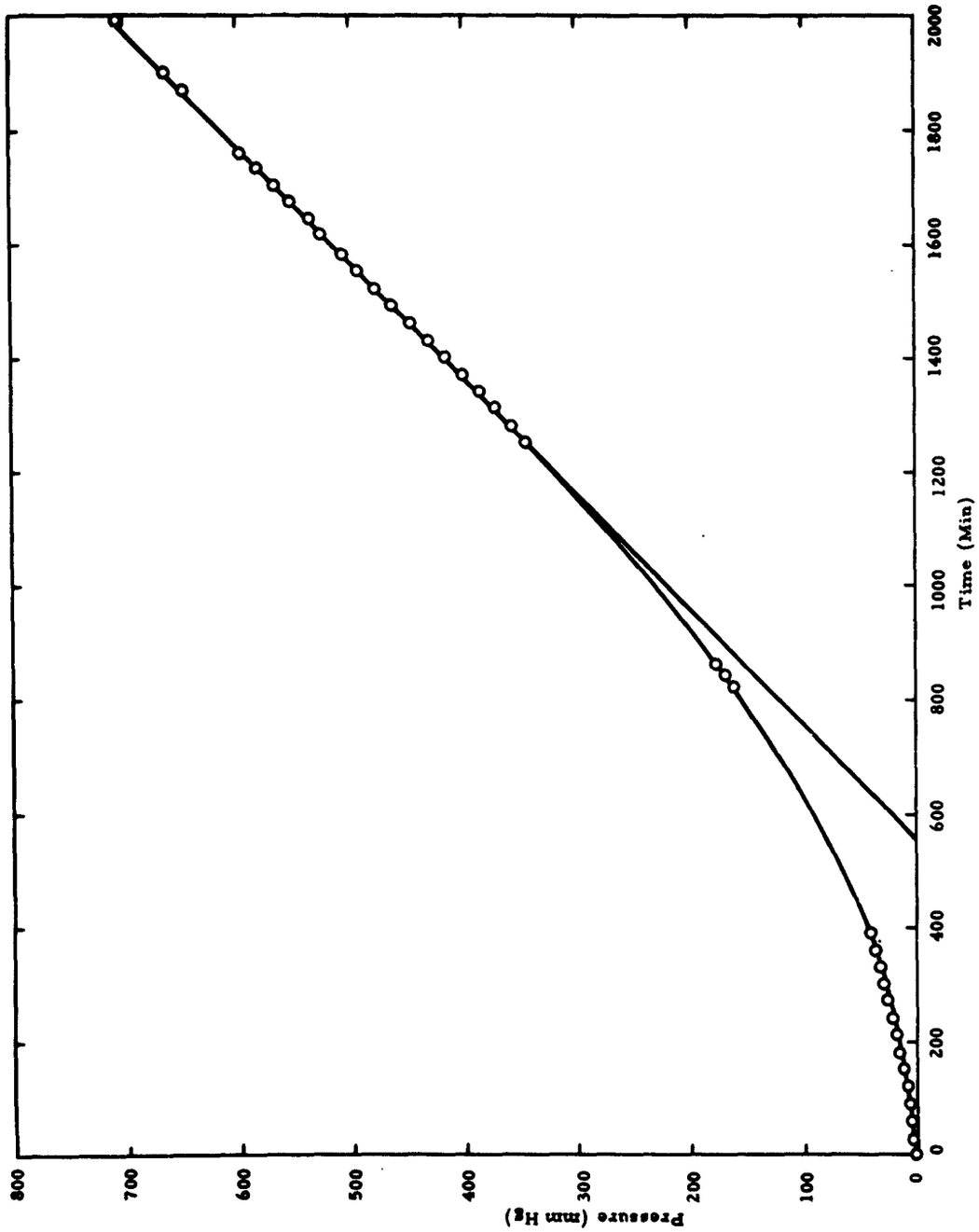

Figure 3. Pressure Versus Time Curve for Hydrazinium Perchlorate at 140°C

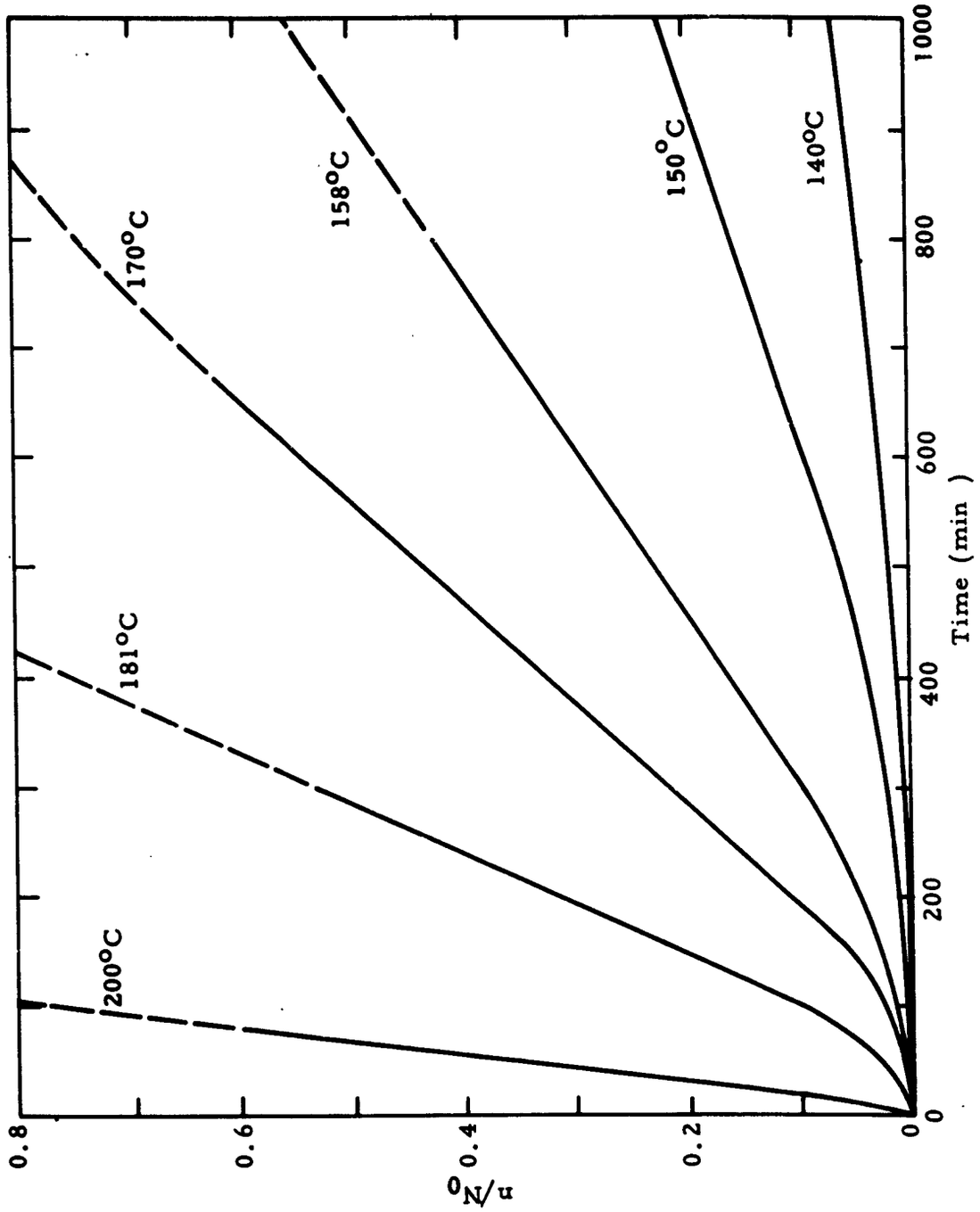

Figure 4. Thermal Decomposition of HP at Various Temperatures

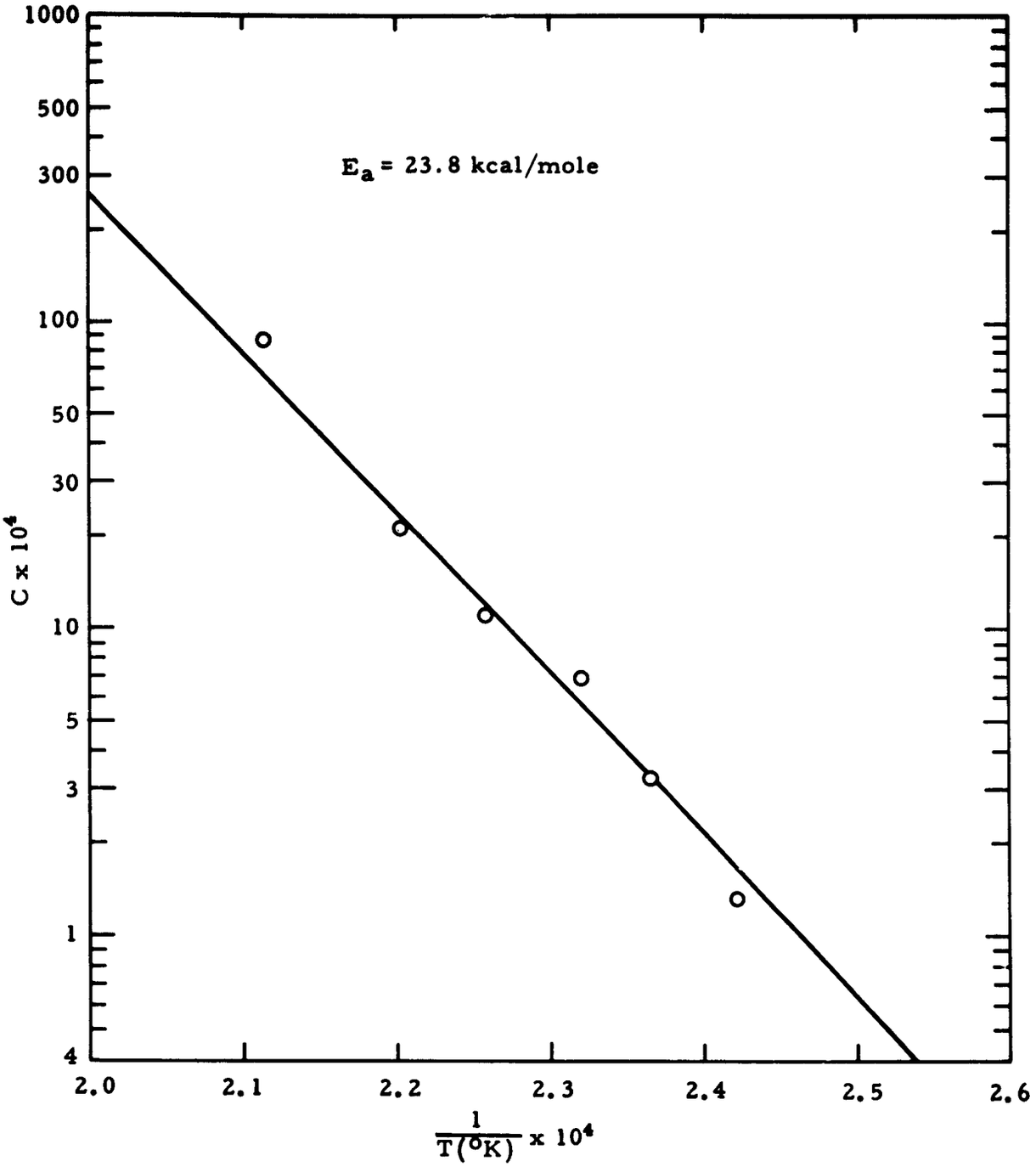

Figure 5. Selected Value of Kinetic Constant C versus $\frac{1}{T(^{o}K)}$

This decrease in the molar ratio of non-condensables to condensables may be a result of an appreciable vapor pressure of reactant or products, or, more likely, a competing reaction path at higher reaction temperatures.

Gases uncondensed at room temperature were analyzed by mass spectrometer, the only species detected in major proportions (> 95 percent) in every case was nitrogen. Traces (< one percent) of hydrogen were also frequently seen. Solid residues were tested for chlorine oxides and nitrogeneous compounds; only NH_4^+ and Cl^- were detected in addition to $N_2H_5^+$ and ClO_4^-.

DISCUSSION

The oxidation of hydrazine in solution by a large variety of oxidizing agents has been extensively studied, the most important theoretical contributions having been made by Kirk and Browne[5], Browne and Shetterly[6], and Cuy and Bray[7]. Depending on the nature of the oxidizing agent(s)

(5) Kirk and Browne, J. Am. Chem. Soc., 50, 337 (1928).

(6) Browne and Shetterly, J. Am. Chem. Soc., 29, 1305 (1907); 30, 53 (1908); 31, 221 (1909); 31, 783 (1909).

(7) Cuy and Bray, J. Am. Chem. Soc., 46, 1786 (1924). Bray and Cuy, J. Am. Chem. Soc., 46, 858 (1924). Cuy, Rosenberg and Bray, J. Am. Chem. Soc., 46, 1796 (1924).

involved, the products contain varying amounts of nitrogen, ammonia, and hydrogen azide. Kirk and Browne showed that oxidizing agents could be placed in three categories: 1) monodelectronators, which gain one electron going from the oxidized to the reduced state; 2) didelectronators, which gain two electrons; and 3) polydelectronators, which go stepwise through intermediate stages involving both monodelectronation and didelectronation.

Monodelectronators oxidize hydrazine to nitrogen and ammonia; the proposed intermediate hydronitrogen is tetrazane. No hydrogen azide is produced by this mechanism, since the unstable intermediate decomposes to ammonia and nitrogen:

$$N_2N\text{-}NH\text{-}NH\text{-}NH_2 \longrightarrow 2NH_3 + N_2$$

Oxidation of hydrazine by didelectronators, especially in strongly acid solution, is assumed to involve formation of N_2H_2 radicals which condense to form tetrazene, isotetrazene or tetrazane. Isotetrazene can then decompose to form hydrogen azide:

$$NH{=}N\text{-}NH\text{-}NH_2 \longrightarrow HN_3 + NH_3$$

The action of polydelectronators is a combination of both reactions and the proportions of N_2, HN_3 and NH_3 produced depends on the intermediate stages of the oxidizing material.

In the thermal decomposition of hydrazinium monoperchlorate, the initial reaction is presumed to be proton transfer with the production of free hydrazine and anhydrous perchloric acid:

$$N_2H_5^+ + ClO_4^- \longrightarrow N_2H_4 + HClO_4$$

The second step is presumed to be decomposition of the acid:

$$HClO_4 \longrightarrow HO^{\cdot} + {}^{\cdot}ClO_3$$

The $\dot{O}H$ radical is a monodelectronator:

$$H\dot{O} + N_2H_4 \longrightarrow \dot{N}_2H_3 + H_2O$$

At these temperatures the hydrazyl radical probably decomposes directly to yield nitrogen and ammonia. Ammonia then displaces hydrazine to produce ammonium perchlorate:

$$\dot{N}_2H_3 \longrightarrow 1/2\ N_2 + NH_3$$

$$NH_3 + N_2H_5^+ \longrightarrow NH_4^+ + N_2H_4$$

The hydrazine is then oxidized by the $\dot{C}lO_3$ radical, also a monodelectronator:

$$N_2H_4 + \dot{C}lO_3 \longrightarrow \dot{N}_2H_3 + HClO_3$$
$$\dot{N}_2H_3 \downarrow NH_3 + 1/2\ N_2$$

Ammonia again displaces hydrazine:

$$NH_3 + N_2H_5^+ \longrightarrow NH_4^+ + N_2H_4$$

Chloric acid, quite unstable even at ambient temperatures, most probably acts as a monodelectronator by immediate decomposition to hydroxyl radical and chlorine dioxide:

$$HOClO_2 \longrightarrow \dot{H}O + \dot{C}lO_2$$

$$\dot{H}O + N_2H_4 \longrightarrow H_2O + \dot{N}_2H_3$$

$$\downarrow$$

$$1/2\ N_2 + NH_3$$

Chlorine dioxide can act as a monodelectronator oxidizing hydrazine to ammonia and nitrogen; ammonia displaces more hydrazine; the chlorous acid produced acts as a monodelectronator, again by decomposition to hydroxyl and hypochloryl radicals, and so forth, until the final monodelectronation produces HCl.

The overall stoichiometry of the reaction appears to be:

$$8\ N_2H_5ClO_4 \longrightarrow 7\ NH_4ClO_4 + NH_4Cl + 4N_2 + 4H_2O$$

This expression is quite consistent with the reaction products found, gives (as closely as can be determined thus far) the correct proportions, and is consistent with the reported theory of hydrazine oxidation. It is very possible that intermediate oxides of chlorine may act as didelectronators to some extent, especially as higher reaction temperatures are studied, thereby producing some hydrogen azide and accounting for the decrease in the ratio of non-condensable gases to condensables.

An approximate kinetic expression based on the preceding theory of the decomposition reaction in which all oxidizing species are presumed to act as monodelectronators reduces to:

$$dn/dt = \frac{[N_2H_4]}{2}\Big[3\,k_1\,[OH] + k_2\,[ClO_3] + 3\,k_3\,[HClO_3] + k_4\,[ClO_2] +$$

$$3\,k_5\,[HClO_2] + k_6\,[ClO] + 3\,k_7\,[HClO] + k_8\,[Cl]\Big]$$

This expression shows qualitatively that the rate of gas evolution should increase until "equilibrium" concentrations of all species are reached,

after which the rate should be constant. Hydrazine is replaced as fast as it is used up by one-for-one displacement by ammonia, whereas the chlorine-based compounds cannot build up to appreciable concentrations due to their inherent instability. The rate-determining step however, is probably the decomposition of anhydrous perchloric acid as indicated by the similarity in activation energies.

Soviet investigators report an activation energy of 22.2 kcal/mole and experiments in our laboratory indicate a value of 22.4-23.1 kcal/mole for the decomposition of the acid, as compared with the value of 23.8 kcal/mole for hydrazinium monoperchlorate as calculated above. Further investigation is obviously to be desired.

APPENDIX A

A REVIEW OF THE THERMAL DECOMPOSITION OF SELECTED SOLID PERCHLORATES

A. INTRODUCTION

This review is concerned with selected solid perchlorate oxidizers which have a nitrogen-containing cation. With one exception, all can be considered as analogs of ammonium perchlorate to a greater or lesser extent. The emphasis has been placed on those characteristics which are supportive to understanding the thermal decomposition reactions of the various compounds. The material treated is taken from both open and classified American sources and from foreign journals and reports. A fairly broad discussion of the various classes of perchlorates and their history is contained in a monograph by Schumacher in 1960 (Ref 1).

Inasmuch as the compounds considered here are for the most part analogs of ammonium perchlorate, names analogous to ammonium perchlorate have been used in discussing them. Certain abbreviations have been used to improve the text where repetition of the full name is unnecessary. A brief tabulation of names, alternate names, formulas, and abbreviations follows:

Abbreviation	Name	Formula	Alternate Name
AP	Ammonium Perchlorate	NH_4ClO_4	-
GP	Guanidinium Perchlorate	$CN_3H_5 \cdot HClO_4$*	Guanidine Perchlorate
HP	Hydrazinium Monoperchlorate	$N_2H_5ClO_4$	Hydrazine Perchlorate
HP-2	Hydrazinium Diperchlorate	$N_2H_6(ClO_4)_2$	Hydrazine Diperchlorate
HAP	Hydroxylammonium Perchlorate	$HONH_3ClO_4$	Hydroxylamine Perchlorate
NP	Nitronium Perchlorate	NO_2ClO_4	Nitryl Perchlorate

* $(NH_2)_2C{=}NH \cdot HClO_4$

B. AMMONIUM PERCHLORATE

1. Preparation and Properties*

Ammonium perchlorate was first synthesized by Serullas (Ref 2) in 1831. A number of methods of synthesis have since been developed, of which, the most common is a double displacement reaction between ammonium chloride and sodium perchlorate. The AP is crystallized from the aqueous solution as the anhydrous salt (Ref 3).

Chemically, AP behaves much like the alkali perchlorates. A strong oxidizer, it is frequently used in explosives and rocket propellants. Its aqueous solutions are slightly acidic because of the common reaction:

$$NH_4^+ + 2H_2O \rightleftharpoons NH_4OH + H_3O^+$$

The crystals are of the orthorhombic class below 240°C, at which temperature a phase change to the cubic class occurs.

The heat of formation of AP at 25°C was reported by Rossini, et al (Ref 4) to be -69.42 kcal/mole. The work of Birky and Hepler (Ref 5) was recalculated by Wagman (Ref 6) who, using more recent values for auxiliary thermochemical data, obtained a value of -70.59 kcal/mole. The most recent reports by Gilliland and Johnson (Ref 7 and 8) indicate a correct value of -70.73 ± 0.32 kcal/mole.

The dissociation pressure for the reaction:

$$NH_4ClO_4 \rightleftharpoons NH_3 + HClO_4$$

between 520°C and 620°C was found by Inami, et al (Ref 9) to follow the relationship:

$$\text{Log P (mm Hg)} = -\frac{6283.7}{T^{\circ}K} + 10.56$$

---

*Only characteristic physical and chemical properties are discussed in the text. A general table of properties can be found in the summary section of this appendix.

The heat of dissociation is reported as 58 ± 2 kcal/mole, as compared with a calculated value (same source) of 59.3 kcal/mole.

2. Thermal Decomposition

The thermal decomposition of AP has been studied periodically since 1868 (Ref 10 through 15). For immediate purposes, however, a brief discussion of the most recent work (i.e., that reported since 1950) is covered.

Bircumshaw and Newman (Ref 16 and 17) studied the kinetics of decomposition of AP in the regions 215°C to 280°C and 380°C to 450°C in 1954. The activation energy for the orthorhombic form was found to be 27.8 kcal/mole and that for the cubic form below 300°C was found to be 18.9 kcal/mole. The characteristic sigmoid curve was obtained for the decomposition at these temperatures, but the reaction proceeded only to 30 percent of the total, leaving a finely divided granular residue of pure AP. The crystals could be "rejuvenated" by exposure to solvent vapor and further decomposed. The curves at these temperatures were fitted quite well by the Prout-Tompkins equations; the acceleratory period could be fitted equally well by the power expression, $p = kt^n$ ($n = 6$), and the deceleratory period by the unimolecular decay law, $-\log (P_{f-p}) = kt + c$. The curves in the higher temperature region were entirely deceleratory; no induction period was detected.

Three possibilities for the decomposition mechanism were considered: (1) proton transfer, which controls sublimation but can also result in decomposition where the molecules produced are unstable species, (2) breakdown of the ions directly, as in the case of alkali metal perchlorates, and (3) electron transfer, producing unstable radicals.

The second possibility (breakdown of the ions directly) was rejected because of the relatively low temperature of the decomposition. Proton transfer was dismissed as resulting in sublimation and was proposed as a possible partial explanation for the termination of decomposition at 30 percent completion. Electron transfer, producing NH_4 and ClO_4 radicals, was proposed as the correct mechanism; this was thought to be confirmed by the effectiveness of such catalysts as MnO_2 and Fe_2O_3, which can act as effective "bridges" in such a mechanism. It was also found that NH_3 absorbed into the crystals is an effective inhibitor of the reaction.

The proton-transfer mechanism, with subsequent decomposition of the free NH_3 and $HClO_4$ produced, was again proposed in 1956 by Schultz and Dekker (Ref 18) who performed theoretical calculations which reproduced the results of Bircumshaw and Newman rather well. Bircumshaw and Phillips (Ref 19), however, performed experiments comparing rates of reaction for AP formed from normal NH_3 and deuterated NH_3; the results did not appear to substantiate the work of Schultz and Dekker. In the same paper, Bircumshaw and Phillips found the activation energy between 400°C and 440°C to be 73.4 ± 1.4 kcal/mole, and the rate-controlling reaction is proposed to be the breakdown of the perchlorate ion. The E_a is compared with that previously obtained for $KClO_4$ by Phillips (Ref 20) 69.3 kcal/mole between 500°C and 550°C. The decomposition of AP between 400°C and 440°C was also reported to go to completion, and the decomposition in the range 300°C to 380°C was found to be irreproducible. The rate of decomposition was also found to be proportional to the pressure of nitrogen used to suppress sublimation.

The irreproducibility of the reaction between 300°C and 350°C was confirmed by Galwey and Jacobs (Ref 21) who explain this pheomenon as a result of competing reactions. The reaction over 400°C was found to be reproducible for both pellets and single crystals, but less for samples preconditioned (30 percent decomposed at lower temperatures). Results were well fitted by the power law, but the index (n) was found to depend on sample mass and temperature to some extent. The contracting cube law:

$$1-(1-\alpha)^{1/3} = kt$$

was found to have wider applicability, and an Arhennius plot gave a value of 38.8 kcal/mole for the activation energy. The mechanism of the high-temperature reaction is proposed to be proton transfer on the surface of the solid, followed by evaporation and decomposition of the $HClO_4$ produced, the fragments of which then oxidize the NH_3 gas. The reaction scheme includes all the products found by Dodé (Ref 15) who represented the overall stoichiometry as:

$$2NH_4ClO_4 \longrightarrow 4H_2O + 2NO + O_2 + Cl_2$$

A subsequent study of the low temperature (<300°C) region by Galwey and Jacobs (Ref 22) confirms the termination of the reaction at about 30 percent decomposition.

The kinetic expression found to fit the plots of Bircumshaw and Newman (Ref 16 and 17) as well as new experimental plots by the authors, is an extremely complicated model derived independently by Avrami (Ref 23) and Erofeyev (Ref 24) in 1941 and 1946, respectively. The 30 percent decomposition is proposed to be decomposition of material relatively loosely held in interstitial positions, which explanation also allows for the differences in E_a for growth of reaction nuclei, which increases in the order: crystal, powder, pellet. The electron transfer mechanism is essentially replaced by a reaction in which molecular AP is formed:

(1) $NH_4^+ + ClO_4^- \longrightarrow NH_4ClO_4$

(2) $NH_4ClO_4 \longrightarrow 2H_2O + N^{\circ} + ClO_2$

The experimental E for growth are 30 kcal/mole and 17 kcal/mole in the orthorhombic and cubic forms, respectively.

The same authors (Ref 25) also treat of the reaction in the region of 450 °C to 500°C, where it reaches a rate bordering thermal explosion. The results, however, are not directly applicable to a further understanding of the thermal decomposition reaction. In another report (Ref 26) in the same year (1960), these authors found that the presence of carbon produces considerable acceleration in the reaction and makes the Avrami-Erofeyev equation no longer applicable. This phenomenon is explained as a result of the absorption of NH_3 produced by the electron transfer mechanism by the carbon. A subsequent study of the reaction between 210°C and 275°C by Raevskii and [illegible] (Ref 27) employing photomicrographic techniques, confirmed the values of E_a obtained by Galwey and Jacobs (Ref 22) by measurement of growth rates of nuclei in single crystals in both orthorhombic and cubic forms, yielding values of 32 $\pm$ 1 and 17 $\pm$ 1 kcal/mole, respectively. The catalysis of the reaction by carbon was explained in terms of an increase in the semiconducting properties of the salt, as the mechanism proposed for the decomposition of the pure AP is an advanced version of the mechanism proposed by Bircumshaw and Newman (Ref 17) i.e.--electron transfer, modified to accommodate the proton transfer mechanism of Galwey and Jacobs (Ref 22).

A number of studies of the effect of impurities on the decomposition rate have been performed. Petricciani, et al (Ref 28) found the reaction to be accelerated by ClO_3^- impurities; Jacobs and Kureishy (Ref 29) found that CuO lowers the thermal explosion temperature by approximately

200°C. Solymosi and Révész (Ref 30) discovered that ZnO accelerates the decomposition, whereas NiO, Fe_2O_3, and CdO were somewhat less effective. The acceleratory effects of x-ray and gamma pre-irradiation were discovered by Freeman, et al (Ref 31); such would be expected from the similar results obtained by Bircumshaw and Phillips (Ref 19) with ultraviolet irradiation.

C. GUANIDINUM PERCHLORATE

1. Preparation and Properties

Guanidinum perchlorate may be prepared by reacting guanidine hydrochloride with a saturated solution of $NaClO_4$ (Ref 32), or by fusion of equivalent amounts of dicyanamide and NH_4ClO_4 at 160°C (Ref 33). Only the slightest data on chemical or physical properties are available; these are found in Table II of the summary section of this appendix.

2. Thermal Decomposition

A thorough study of the thermal decomposition of GP was made by Glasner and Makovky (Ref 32, 34, and 35) about 10 years ago. Below 300°C there appeared to be no appreciable decomposition even after several hours. Above 320°C, the molten material gradually undergoes a change to a yellow, waxy solid. This is separable into three fractions: NH_4ClO_4; a mixture of perchlorlates of melamine; and ammeline, melam, and mellon. If the reaction is allowed to proceed, it goes to completion.

The apparent sequence of reactions is:

(1) $CH_5N_3 \cdot HClO_4 \longrightarrow NH_2CN + NH_4ClO_4$

(2) $3NH_2CN \longrightarrow C_3H_6N_6$ (melamine)

(3) $NH_4ClO_4 \longrightarrow NH_3 + HClO_4$

(4) $C_3H_6N_7 + HClO_4 \longrightarrow$ Gaseous products

The overall reaction corresponds to two equations:

(a) $2CH_5N_3 \cdot HClO_4 \longrightarrow 2HCl + 5H_2O + CO + CO_2 + 3N_2$

(b) $2CH_5N_3 \cdot HClO_4 \longrightarrow 2HCl + 2H_2O + O_2 + 2CO_2 + 2N_2 + 2NH_3$

The relative importance of these two stoichiometries is related to the temperature, higher temperatures favoring reaction (a). At lower temperatures the NH_3 in the vapor phase is less subject to oxidation by $HClO_4$ since the latter is less volatile than NH_3. The dissociation of NH_4ClO_4 appears to be related to the glass surface area, since Pyrex glass acts as a catalyst to some extent. Addition of 10 percent powdered Pyrex glass to the GP leads to a pyrolysis, such that the reaction is zero order with respect to GP. That molecular $HClO_4$ is the oxidizing agent, as opposed to the ClO_4^- ion, is indicated by that facts that: (a) mixtures of GP and AP have the same decomposition rate (measured manometrically) as GP alone, (b) pure GP has an induction period (during which the yellow, waxy solid forms), whereas mixtures of GP and AP have none, and (c) mixtures of GP and $KClO_4$ exhibit very slow reaction rates. Thus, the rate of the reaction measured manometrically should be directly related to the rate of dissociation of NH_4ClO_4 on the walls of the reaction vessel.

The typical curve found by these investigators (percent gas evolved versus time) begins slowly, up to about 15 percent, then rises linearly up to about 80 percent after which near-explosion terminates the reaction. The induction period (0 to 15 percent) is believed to represent a predominance of reaction (a) of the mechanism proposed. The second phase, a constant rise in percent gas evolved versus time, is explained on the basis of a steady concentration of the intermediates $HClO_4$. The last, almost explosive phase is considered to be caused by a large excess of $HClO_4$ with respect to the organic materials. As a comparison, equimolar mixtures of dicyandiamide with AP and of quanidine chloride with AP give points falling quite close to those for pure GP at the same temperature. Thus, it is confirmed that reaction (1) cannot be rate-determining, and that reaction (3) probably is. The steady state approximation for the $HClO_4$ concentration is also supported.

The catalytic effects of some dry metal oxides were also studied. Three general classes are defined as follows:

a. Alkali and alkaline earth oxides exert a slight acceleratory influence, but do not change the character of the pyrolysis.

b. Oxides of transition metals have a more pronounced acceleratory effect and may cause deflagration or even explosion at fairly low temperatures.

c. Some specific metal oxides and metals (V_2O_5, Fe_2O_3, CuO, Pt foil) cause an explosion at any temperature above 300°C. These probably greatly accelerate the decomposition of the NH_3 present, thus contributing an additional acceleratory effect to the process. Further evidence that NH_3 decomposition is involved in explosions of catalyzed GP is found in the fact that the same materials cause explosion with AP, although at higher temperatures.

The rate constant for the middle phase of the decomposition (linear rise) may be expressed by the equation $k = 2.4 \times 10^{11} e^{-32400/RT}$ %/min. When log of induction period is plotted against reciprocal absolute temperature, the activation energies for GP and AP are found to be 30.5 kcal/mole and 31.5 kcal/mole, respectively. (This part of the study was performed in the temperature range 390°C to 440°C for GP and 440°C to 480°C for AP. In this range, GP ignites after a definite induction period, and reaction ends leaving a yellow residue, probably mellon.) The activation energies (from induction period and from zero order decomposition), it is most interesting to note, is 31.3 kcal/mole, the same as the E_a obtained for AP (Ref 22).

D. HYDRAZINUM MONOPERCHLORATE

1. Preparation and Properties

Hydrazinium monoperchlorate was first made by Salvadori (Ref 36) by neutralizing a dilute solution of hydrazine with dilute perchloric acid. The compound formed is the hemi-hydrate, $N_2H_5ClO_4 \cdot 1/2H_2O$, which is stable up to 60.5°C. The anhydrous salt can be re-crystallized from alcohol. The hydrate is less sensitive to detonation by shock than the anhydrous compound.

A brief comparison (Ref 37) of the solubility of HP in water and absolute ethanol is shown below. HP is insoluble in ether, carbon tetrachloride, trichloroethylene, benzene, chloroform, and carbon disulfide.

Temp (°C)	Grams HP/100 grams solution Water	Ethanol
0	23.4	v. slight
40	68.9	---
60	87.4	69.0
75	93.1	---

According to a recent Soviet report (Ref 38), the heat of formation at 25°C is -42.9°C, based on a heat of solution of 9.77 kcal/mole for 1:1000 dilution in water (compare Gilbert, Ref 39: 9.26 kcal/mole) and the heats of formation for aqueous ClO_4^- and $N_2H_5^+$ reported by Rossini, et al, Ref 4, (-31.41 and -1.7 kcal/mole, respectively).

2. Thermal Decomposition

Salvadori (Ref 36) has noted that on prolonged heating of solid HP below its melting point (131-132°C) the compound decomposes. The rate of decomposition rapidly increases with temperature and an explosion occurs at 240°C. Barlot (Ref 37) has reported that the perchlorate melts at 137°C to 138°C and begins to decompose at 145°C with complete decomposition taking place at 230°C. Salvadori also indicates that when ignited HP burns without detonation and explodes on impact or when initiated with mercury fulminate.

Schidlovskii, et al (Ref 38) found a melting point of 140.5°C to 141.0°C. The impact sensitivity was somewhat greater than that for TEN: with a five kg weight and 15 cm height TEN gave 68 percent explosions in the ball-drop test. Under the same conditions, the detonation level of HP was 88 percent. Hydrazinium monoperchlorate is very sensitive to friction; it detonates when rubbed slightly in a porcelain mortar. Measurements in a lead block with a 10 gm sample gave an expansion of 383 and 388 cm^3.

Schidlovskii, et al (Ref 38) determined the thermal stability by measuring the weight loss of a 0.2 gm sample after six minutes at a fixed temperature. The following table gives these values.

WEIGHT LOSS AFTER SIX MINUTES

Temp (°C)	Loss (%)
160	Negligible
180	0.3
200	0.7
220	3.1
240	5.4
250	Rapid Consumption

Determination of the thermal ignition (bath of Wood's metal, heating at 20°/min from $100^{\circ}C$) gave a fume-off at $277^{\circ}C$ to $280^{\circ}C$ with a 0.2 gm sample. Under comparable conditions, NH_4ClO_4 had a fume-off above $360^{\circ}C$. Thus, HP is thermally much less stable than NH_4ClO_4.

Addition of five percent MnO_2 lowered the fume-off to $254^{\circ}C$ to $259^{\circ}C$; five percent $CuCl_2$ produced a violent detonation at about $170^{\circ}C$.

E. HYDRAZINIUM DIPERCHLORATE

1. Preparation and Properties

The diacid salts of hydrazine, such as $N_2H_4 \cdot 2HClO_4$ are prepared readily by crystallization from aqueous solutions containing an excess of the acid. This results in the dihydrate, $N_2H_4 \cdot 2HClO_4 \cdot 2H_2O$ which must be dehydrated. This is conviently accomplished by digestion with 70 percent $HClO_4$ at room temperature, filtering off the solid, and vacuum drying at a somewhat elevated temperature.

Hydrazine diperchlorate is a very hygroscopic, white crystalline solid of molecular weight 232.98. It forms a dihydrate $N_2H_6ClO_4 \cdot 2H_2O$ whose vapor pressure on dissociation is given by (Ref 40):

$$\log P_{(mm)} = 11.77 - \frac{3850}{T} \qquad (80^{\circ}C \text{ to } 120^{\circ}C)$$

On heating, dissociation takes place according to the equations:

$$N_2H_4 \cdot 2HClO_4 \rightleftharpoons N_2H_4 \cdot HClO_4 + HClO_4$$

$$\log P_{(mm)} = 22.86 - \frac{8650}{T} \qquad (100^{\circ}C \text{ to } 140^{\circ}C)$$

The heat of dissociation for the HP-2 determined from the pressure-temperature relationship is -37 kcal/mole.

A study made at the Allegany Ballistics Laboratory (Ref 41) reported the heat of formation as $\Delta H_f^{o} = -92.55$ kcal/mole. More recently a value of -77 kcal/mole was calculated from theoretical considerations (Ref 42). Studies at Thiokol Chemical Corp., RMD, led to a value of $\Delta H_f^{o} = -69.9 \pm 0.3$ kcal/mole.

2. Thermal Decomposition

HP-2 decomposes according to the equation:

$$12N_2H_6(ClO_4)_2 \longrightarrow 4NH_4ClO_4 + 12HClO_4 + 22H_2O + 10N_2 + 5O_2 + 4Cl_2.$$

In addition, traces of H_2, HCl and NO or NO_2 were detected by mass spectrometry. The major investigations on HP-2 were performed at RMD.

The characteristic P versus t curve at 140°C begins with a sharp rise to about 90 mm Hg (dissociation pressure at 140°C), followed by a slow pressure rise (rate varies) and terminating in a sudden sharp rise in pressure too fast for the apparatus to follow. It has been reported that the average time to decomposition (accelerated phase) is approximately 24 hours at 140°C, however, this is variable and depends upon many considerations. Metals and metal ions, especially iron, act as catalysts for the induction period, as does $HClO_4 \cdot 2H_2O$ (induction time is inversely proportional to concentration of dihydrate), whereas a slight percentage of NH_3 greatly extends the induction period. Perchloric acid in the anhydrous state shortens the induction period considerably.

Experiments at 130°C succeeded in trapping out $HClO_4$, and recovery of the residual solid gave an excellent mass balance with the $HClO_4$ produced. Another experiment, in which trapped $HClO_4$ was allowed to vaporize and come in contact with the residual solid (at room temperature), gave almost 100 percent recovery of the original HP-2 sample. These experiments lead to the assumption that the initial reaction is simple dissociation:

$$HP\text{-}2\ (s) \longrightarrow HClO_4\ (v) + HP\ (s)$$

This is the reaction which occurs in the initial rise to "equilibrium" vapor pressure. Based on the assumption that no decomposition occurs in the vapor state, the dissociation apparently will proceed only to about 11 to 12 percent maximum, but if the residual solid is cooled and allowed to stand for a time, reheating to 140°C will remove additional $HClO_4$. Some relationship between induction period and sample mass has been observed, but this may be affected by variations in sample geometry. The energy of activation, from induction periods at various temperatures, is 23.5 kcal/mole.

Material has been maintained for over a year at RMD at 70°C without deflagration; other samples analyzed after more than a year at room temperature showed little decomposition.

F. HYDROXYLAMMONIUM PERCHLORATE

1. Preparation and Properties

Hydroxylammonium perchlorate was first reported in a U. S. patent by Robson (Ref 43) who prepared it by the reaction:

$$2HONH_3Cl + Ba(ClO_4)_2 \xrightarrow{EtOH} BaCl_2 + 2(NH_3OH)ClO_4$$

Zinov'ev and Zakharova (Ref 44) prepared HAP by reacting $(NH_3OH)_2SO_4$ with $Ba(ClO_4)_2$ to give $(NH_3OH)ClO_4$ and $BaSO_4$.

HAP was found to be soluble in alcohol and acetone, less in dichloroethane and diethyl ether, and almost insoluble in benzene, toluene, and carbon tetrachloride.

Rocchicioli (Ref 45) reported, on the basis of infrared analysis, the presence of the hydroxylammonium ion and the perchlorate ion.

2. Thermal Decomposition

It was found by Soviet scientists (Ref 44) that HAP was unstable to shock and friction. Thermal analysis showed two exotherms and one endotherm, and the former at 178°C to 220°C and 313°C to 370°C, and the latter commencing at 520°C. They believed the 180°C exotherm was the decomposition of HAP as expressed in the following equation:

$$(NH_3OH)ClO_4 = NH_4ClO_4 + 0.5O_2$$

The resulting ammonium perchlorate then decomposed at 315°C. The endothermic effect is caused by the sublimation of ammonium chloride, one of the products of the process.

Thiokol Chemical Corporation (Ref 46) work reported an estimated activation energy of thermal decomposition of 38 kcal/mole. The reaction was accelerated by pressure but was not autocatalytic. A heat of vaporization was found to be 33 kcal/mole.

G. NITRONIUM PERCHLORATE

1. Preparation and Properties

Hantzsch (Ref 47) was the first to synthesize nitronium perchlorate, but he erringly reported it as $NO(OH)_2ClO_4$. Later Goddard, et al (Ref 48) identified Hantzsch's material as a mixture of NO_2ClO_4 and OH_3ClO_4. NP was first prepared in the pure state by Gordon and Spinks (Ref 49) who mixed ClO_2 with ozone and various oxides of nitrogen.

Another method of preparing NP is by mixing anhydrous perchloric acid with N_2O_5 as given by the following equation (Ref 50):

$$N_2O_5 + 3HClO_4 = 2(NO_2^+)(ClO_4^-) + (H_3O^+)(ClO_4^-)$$

$$(H_3O^+)(ClO_4^-) + 2N_2O_5 = (NO_2^+)(ClO_4^-) + 3HNO_3$$

A white monoclinic (Ref 51) solid, composed of NO_2^+ and ClO_4^- ions, (Ref 52) NP is soluble in nitric acid, slightly soluble in CH_3NO_2 and CCl_4, and extremely hygroscopic (forming HNO_3 and $HClO_4$) at normal temperatures. NP reacts with H_2SO_4 at cryogenic temperatures (Ref 53) according to the equation:

$$NO_2ClO_4 + H_2SO_4 \longrightarrow NO_2^+ + HClO_4 + HSO_4^-$$

Work by Cordes and Fetter (Ref 54) in 1958 indicated a heat of formation of +8.10 kcal/mole calculated from the heat of reaction with water. More recent work at National Bureau of Standards by Gilliland (Ref 55) and at Callery Chemical Company (Ref 56) indicated heats of formation of +8.88 kcal/mole and +8.74 kcal/mole, respectively. Using more recent values for auxiliary heats of formation, Gilliland recalculated Cordes' data of 1958 and arrived at +8.74 kcal/mole, in excellent agreement with his own work.

2. Thermal Decomposition

The rate of isothermal decomposition of NP was measured in two independent investigations in 1959-1960. Biddle et al (Ref 57) working in the range 97°C to 155°C, found the characteristic sigmoid curve reported for AP by Bircumshaw and Newman (Ref 58) but also reported a rather definite dependency on sample mass. Using the relationship:

$$= + \frac{\log t' \, 1/2 - \log t \, 1/2}{\log W_1 - \log W'_1}$$

the order n can be calculated as 1.4 for the linear portion of the curve. Fair agreement with this value was obtained between 107°C to 127°C. By measuring the slope ($d(\frac{PV}{W_i})/dt$) of the linear portions of the curves for a series of runs at various T, and plotting versus 1000/T°K, the agreement for runs of comparable initial masses is quite good, E_a was found to be 17 kcal/mole as compared with 30.4 kcal/mole for a similar treatment of AP below 240°C (crystal transition point). See Reference 58. Cordes (Ref 59) was also engaged in the study of isothermal decomposition of NP at 116.9°C. The stoichiometry based on the total moles of chlorine trapped is:

$$NO_2ClO_4 \longrightarrow 1/2\ N_2O_5 + 1/4\ ClO_2 + 3/2\ O_2 + 3/8\ Cl_2$$

A series of runs were made starting with a vacuum in which sample masses varied from 0.14 gm to 0.31 gm. The rate data was reduced to units of fractional decomposition (α) per unit time. It was found that all samples gave nearly identical curves of α versus t or $d\alpha/dt$ versus t. The variation between $d\alpha/dt$ at a given α for various runs was about 15 percent and independent of sample mass. A graph of $d\alpha/dt$ versus α reproduced in the report shows that the rate starts rather low, rises to a maximum at about 1100 seconds ($\alpha = 0.2$) and then declines. Other runs were made in presence of 25 to 50 mm of added O_2 or N_2, which strongly accelerated the rate independent of the initial gas pressure and nature of the gas. The position of maximum rate remained at $\alpha = 0.2$. Cordes notes that the reaction rate should depend on sample size since larger samples, which decompose at the same initial rate, produce more gas than smaller samples, thereby increasing the pressure and accelerating the reaction. In his technique, however, the product gases were frozen out as generated; this pressure-acceleration phenomenon is in agreement with the findings of Biddle, et al (Ref 57) who do not mention freezing out decomposition products. Cordes also notes that the past history of any given sample batch affects kinetic data greatly, especially with regard to impurities and particle sizes.

In 1960, successive reports by Cordes (Ref 60 and 61) relate results of runs made without trapping out products. The total moles evolved for the untrapped runs was 2.97 to 3.00 per mole of solid as compared with 2.96 moles/mole solid in trapped runs. In addition, the pressure in the system remained constant after a run was stopped, indicating reasonable stability for the products late in a run. In experiments with all products except O_2 trapped out the pressure behavior was as follows: a rapid rise in rate from zero to eight percent decomposed, a decline to a minimum at 16 percent decomposition, and another rise to a second maximum at 28 percent decomposition. The inflections are not

pronounced and the rate could be considered a constant in this region; however, two separate runs are in agreement with respect to the position of inflections. The difference between the maxima and the minimum rates (20×10^{-6}/sec in $d\alpha/dt$) is nearly within experimental error. When no products are trapped out, the rate curve is identical (up to eight percent decomposition) with rates for the trapped runs. The rate then continues to rise to a maximum at 16 percent decomposition, then decreases to cross the curve for trapped runs at about 24 percent decomposition. Beyond 30 percent decomposition, the rate is below and nearly parallel to that for the trapped runs. Cordes poses as explanation for these peculiarities the possibility of 10 to 15 percent $NOClO_4$ as impurity in the initial material, citing similarity to results of decomposition of impure material obtained by Thiokol Chemical Corporation (Ref 57). By a "predecomposition" treatment (referred to also as "superdrying"), Thiokol's Biddle and coworkers obtained rates for pure NP, which do not agree with Cordes' data, as he notes here. Other runs by Cordes indicate that O_2 (or any other gas) accelerates the rate late in the run but this does not occur after the maximum position has been attained. The initial pressure does not appear to affect the supposed decomposition of the NOClO. impurity however.

In the second report cited above, Cordes reports gathering rate data at 117°C, 112°C, and 107°C. These data are consistent with the following mechanism:

1. Nuclei are formed from active centers in a process which is first order in the active centers. There is a limited number of active centers and they are used up as nuclei are formed.

2. The nuclei formed grow linearly with time.

3. The growing nuclei terminate in a process which is first order in the nuclei. The differential equation derived from this mechanism is:

$$\frac{d\alpha}{dt} = KNo^* \left(1 - e^{-k_1 t}\right) - k_3$$

α = fraction decomposed

KNo^* = a measure of the linear growth rate

k_i = nucleation constant

k_3 = termination constant

This equation fits the data at all three temperatures. The constants decrease with decreasing temperature. At the lower two temperatures, $KNo^* = k_3$ numerically, whereas at 117°C $KNo^* > k_3$. The process beyond the occurrence of the maximum rate is first order with respect to the NP remaining.

A more recent report by Biddle, et al (Ref 62) notes a gradual exotherm at about 115°C, a rapid endotherm at 148°C, and an equally rapid exotherm at 156°C after which the sample has been completely consumed. The previously cited work on E_a is mentioned, with the added remarks that plots of rates of individual reactions were "typical of the type found for decay of intermediates in first-order reactions," and, "this can be explained by assuming activated centers of decomposition during the course of the reaction." This last quote is strongly reminiscent of AP work cited in this review.

A plot of vapor pressure versus reciprocal T°K included in the cited report appears to consist of two sections, one between 10°C and 45°C, said to represent sublimation, and another above 45°C to 80°C, representing combined sublimation and decomposition. ΔH_{sub} from the lower portion is 18 kcal/mole; from the upper portion it would be 27 kcal/mole. It is reasonable that the two processes go on simultaneously, since the E_a = 17 and ΔH_{sub} = 18. The sample of NP used was of very high purity. The 27 kcal/mole heat of sublimation represents a statistical combination of the heat of sublimation (18 kcal/mole) and the heat of reaction for the decomposition. It was also found that irradiation by UV (3000-4500°A) led to significant decomposition over an extended period.

Work done at RMD (Ref 63) in 1963 on "superdried" and "non-superdried" NP found that preconditioning (pumping down under high vacuum at room temperature or at 40°C) for several hours apparently removed some inhibiting material originally present. Non-preconditioned samples required twice the time to enter the accelerated phase (appearance of red-brown vapors) as did preconditioned material. Free vapor space does not seem to affect the induction time particularly, except in the area of one to 10 cc/gm, when pressure effects noted above become apparent. Decomposition rates are shown below:

T (°C)	Superdried (%/hr)	Non-superdried (%/hr)
40	0.005×10^{-3}	0.6×10^{-3}
50	0.013×10^{-3}	3×10^{-3}
60	0.12×10^{-3}	10×10^{-3}
70	1×10^{-3}	50×10^{-3}

(These refer to the portion of the process before acceleration.)

Spot tests on the residue, after the induction period was over, showed the presence of NOP (nitrosyl perchlorate, $NOClO_4$). This, coupled with mass spectral analysis of gaseous products, suggested the following mechanism:

$$2NO_2ClO_4 \longrightarrow 2NOClO_4 + O_2$$

$$2NOClO_4 \longrightarrow NO_2ClO_4 + NO_2 + 1/2\ Cl_2 + O_2$$

$$2NO_2ClO_4 \longrightarrow 2NOClO_4 + O_2, \text{ and so forth.}$$

Moisture appears to catalyze the decomposition to some extent, as does air pressure (moisture causes hydrolysis, producing HNO_3 and $HClO_4$). The rapid rate of decomposition is not reached even after several months below 70°C, but at 70°C, induction times (ti) equals 90 hours for preconditioned, superdried samples and 200 hours for non-preconditioned , superdried material.

The most recent information on NP is Cordes' paper (Ref 64) of August 1963, in which the thermal decomposition of NP is examined in the range 69.99°C to 112.3°C. Cordes finds no relation of rate of decomposition to initial sample size (mass) when rate is measured as α . Plots of α versus time are not smooth nor exactly repeatable, but a $d\alpha/dt$ versus t gives a repeatable curve. The analysis of the data using the theory of K. L. Mampel (Ref 65) gives rate constants for initiation of nuclei of decomposition

$$k_1 = 10^{12.6\pm0.5} e^{-28.5\pm0.8/RT} \text{ sec}^{-1}$$

and growth of nuclei

$$k_2 = 10^{12.5\pm0.6} e^{-27.5\pm0.9/RT} \text{ sec}^{-1}$$

and the induction time

$$t_i = 10^{-15.0\pm0.9} e^{30.7\pm1.5/RT} \text{ sec}$$

Cordes finds an excellent fit of theoretical curve to experimental curve between five percent and 95 percent decomposition. He does express some slight reservations about the theory regarding the effect of particle size, and suggests possible modifications.

H. SUMMARY

The order of decreasing thermal stability among the compounds discussed in this review appears to be:

$$NH_4ClO_4 > HN = C(NH_2)_2 \cdot HClO_4 > N_2H_5ClO_4 = HONH_3ClO_4 > N_2H_6(ClO_4)_2 > NO_2ClO_4$$

Exact comparisons are not possible in all cases since studies were not performed under the same conditions.

It would appear, from structural considerations, that these compounds fall into two distinct groups: (1) Ammine-type salts (containing the structural entity $HClO_4$), and (2) NO_2ClO_4, which does not contain the "perchloric acid molecule." Since the ClO_4^- ion does not appear to be the oxidizing agent acting in these decompositions (viz. Section C), and since dissociation of the type $RNH_3X \longrightarrow RNH_2 + HX$ is so commonly experienced, it is only reasonable to suppose that the decomposition reaction follows a path of the following type:

(a) $RNH_3ClO_4 \rightleftarrows RNH_2 + HClO_4$

(b) $HClO_4 \longrightarrow HO^{\cdot} + {}^{\cdot}ClO_3$ (or other strong-oxidizer products)

(c) $HO^{\cdot} + RNH_2 \longrightarrow$ products

(d) ${}^{\cdot}ClO_3 + RNH_2 \longrightarrow$ products

The possibilities of chain-branching, autocatalysis, surface effects, and so forth, are great in such a system, and depend on the nature of the group designated "R".

Some justification for this supposition is found in Table I, wherein standard heats of formation, heats of neutralization in aqueous solution, and heats of neutralization (anhydrous) are compared. The compounds are listed in order of decreasing stability.

TABLE I

RELATIONSHIP OF THERMAL STABILITY
TO CERTAIN THERMODYNAMIC PROPERTIES

Salt (in order of decreasing stability)	$\Delta H^{o}_{f_{298}}$	ΔH neut. (aq)*	ΔH neut. (anh.)
NH_4ClO_4	-70.73	-25.5	-40.31
$HONH_3ClO_4$	-66.5	---	-29.9
$N_2H_5ClO_4$	-42.9	- 9.88	-43.9
$N_2H_6(ClO_4)_2$	-66.9**	- 5.36**	-12.9**

*Based on the reaction $B + HClO_4 \xrightarrow{Aq} BH^+ + ClO_4^-$
**Based on the reaction $N_2H_5ClO_4 + HClO_4 \longrightarrow N_2H_6^{++} + 2ClO_4^-$

The dissociation:

$$N_2H_6(ClO_4)_2 \longrightarrow N_2H_5ClO_4 + HClO_4$$

has been experimentally verified (viz. Section E), and analogous dissociations have been proposed independently in predicated mechanisms for ammonium perchlorate and guanidinium perchlorate.

Additional information has been tabulated in Table II to facilitate comparisons of the physical and thermodynamic properties of these compounds.

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TABLE II

SELECTED PROPERTIES OF PERCHLORATE SALTS

Name	Ammonium	Guanidinium	Hydrazinium (1)	Hydrazinium (2)	Hydroxyl-ammonium	Nitronium
Code	AP	GP	HP	HP-2	HAP	NP
Formula	NH_4ClO_4	$HN{=}C(NH_2)_2 \cdot HClO_4$	$N_2H_5ClO_4$	$N_2H_6(ClO_4)_2$	$HONH_3ClO_4$	NO_2ClO_4
Character	$NH_4^+ \ ClO_4^-$		$N_2H_5^+ \ ClO_4^-$		$HONH_3^+ \ ClO_4^-$	$NO_2^+ \ ClO_4^-$
Mol. wt.	117.5	159.5	132.5	233.0	133.5	145.5
Density	1.95		1.927	1.86	2.02	2.25
Melt. Point	d	240°C	140.5°C		100° C	d
ΔH_f^o	-70.73		-42.9	-69.9	-66.5	+8.88
ΔH_s					33	18
Autoignition Temp	290°C			150°-160°C		147°C
Hygroscopicity				Very. Forms $\cdot 2H_2O$	5.6% R.H. (Pract.)	Hydrolyzes to HNO_3 + $HClO_4$
Crystal Habit	Rhombic < 240°C Cubic 240°C		App. Monoclinic		App. Monoclinic	Monoclinic
Color	White	White	White	White	White	White
Refr. Index	1.4824 1.4828 < 240°C 1.4868 --- 1.4828 > 240°C					
Dimensions						a= 9.25A° b= 6.93A° c= 7.34A° B= 115.5°
Remarks			Impact, friction and spark sensitive			

APPENDIX B

THE THERMAL DECOMPOSITION OF HYDROXYLAMMONIUM PERCHLORATE

A. INTRODUCTION

Hydroxylammonium perchlorate was first reported in a US patent by Robson (Ref 1 and 2) in 1956; a non-aqueous preparation is given, with no details as to physical or chemical properties other than the melting point (87.5 to 90°C), drop weight value (15 cm), and initial decomposition temperature (120°C). More recently, Zinov'ev and Zakharova (Ref 3) issued a paper claiming to have carried out preliminary studies on the compound in 1954. The preparation from hydroxylammonium sulfate and barium perchlorate in aqueous solution is described, as well as an unsuccessful attempt to prepare the material from perchloric acid dihydrate and hydroxylamine hydrochloride. Qualitative solubility studies in organic solvents are described, and a rather approximate guess at the stoichiometry of reaction is made on the basis of comparison of DTA experiments with others performed on ammonium perchlorate. The product gases, evolving first at about 180°C, are said to be neutral and mainly oxygen, leading to the expression:

$$(NH_3OH)ClO_4 \longrightarrow NH_4ClO_4 + 0.5\ O_2$$

Infrared analysis reported by Rocchiccioli (Ref 4) indicates the ionic character of the salt by characteristic $HONH_3^+$ and ClO_4^- bands.

Research on hydroxylammonium perchlorate carried out at Thiokol's Elkton Division (Ref 5) in 1963 indicated that the method of preparation patented by Robson is still best. Vapor pressure studies by the Langmuir technique and the Knudsen technique indicate vapor pressures ranging from 10^{-2} to 10μ Hg between 95°C and 160°C, with a variance of a factor of 10 between the two techniques. The heat of vaporization by the Langmuir technique is 32.3 kcal/mole, that obtained by the Knudsen technique is 33.5 kcal/mole, in excellent agreement. Studies of the products of thermal decomposition of hydroxylammonium perchlorate by mass spectral means have shown "no significant decomposition" at 150°C for one hour. At temperatures in excess of 200°C, a complex mixture of gases is detected above the sample; the simple decomposition into ammonium perchlorate and oxygen reported by Zinov'ev and Zakharova was not detected, but ammonium perchlorate has been found as a residue of DTA studies. A rather good set of DTA thermograms is reproduced, each showing a melting endotherm, solvent impurity endotherm and a deflagration exotherm. The precise location of these peaks depends on the

heating rate and, to some slight extent, the concentration of impurity; at 4.5°C/minute, the impurity peak occurs at 65°C, the melt peak at 88°C, and the deflagration form 190°C to 206°C (the maximum).

This work was performed to further elucidate the kinetic parameters, stoichiometry, and mechanism of decomposition of hydroxylammonium perchlorate as part of a general study of the thermal decomposition of ammoniacal salts of perchloric acid.

B. EXPERIMENTAL

1. Preparation

Several variations on the method of Robson, as well as the original, have been employed in the preparation of hydroxylammonium perchlorate in small quantities. The method as patented consists of the reaction between equivalent amounts of hydroxylamine hydrochloride and barium perchlorate in absolute ethanol.

$$2HONH_3Cl + Ba(ClO_4)_2 \xrightarrow[\text{abs}]{EtOH} 2HONH_3ClO_4 + \underline{BaCl_2}$$

The reaction is carried to completion by the precipitation of insoluble barium chloride which is then filtered out. The ethanol is evaporated, leaving the perchlorate contaminated with any excess of either reagent. These impurities are removed by redissolving the product in anhydrous diethyl ether, in which both the hydrochloride and $Ba(ClO_4)_2$ are insoluble and may be removed by filtration. The hydroxylammonium perchlorate is then reprecipitated from the ether solution by addition of anhydrous benzene. The purification with ether is repeated, and the salt again reprecipitated by addition of benzene.

Material produced in this manner gave assays ranging from 92 to 96 percent, depending on duration of drying at a pressure of 0.05 mm Hg at ambient temperatures by titration with NaOH solution to the phenolphthalien end point. Drying at temperatures above 50°C resulted in degradation of the occluded solvent and contamination by the products of the degradation.

To improve the purity of the product, the first variation on Robson's method examined was the elimination of the reprecipitation with benzene. After redissolving in ether and filtration, the solution is taken to dryness at ambient temperature in a flash evaporator at a pressure of 0.05 mm Hg. Pumping is

continued for a period of six hours, after which the material assays 98 to 99 percent by titration. Material produced in this manner has been used in decomposition studies to date.

Inasmuch as the material produced by aqueous methods exhibits a very slight variation in the deflagration exotherm on a DTA thermogram, some of our product was redissolved in water (the aroma of ether was immediately detected) to provide an "aqueous" sample for comparative decomposition studies. The solution was taken to dryness in the flash evaporator, dried in a vacuum oven for 24 hours at 64°C, and analyzed; the purity was 89 percent by titration. Another batch was subjected to vacuum drying at a pressure of 0.05 mm Hg for seven hours at 70°C. The product of this extended drying assayed 97.5 percent. This latter drying was performed in a special drying tube with constant agitation of the solid to prevent caking and agglomeration.

2. Apparatus

The vapor pressure study on the 89 percent pure aqueous sample and the thermal decomposition studies on the 98.5 percent pure non-aqueous sample were performed in sickle gauges previously described. Samples are subjected to a vacuum of 0.005 mm Hg for 30 minutes prior to sealing. The experiment is conducted in the same manner as those performed on hydrazinium monoperchlorate.

C. RESULTS

1. Vapor Pressure of 89 Percent Pure Aqueous Sample

0.100 gm of 89 percent pure aqueous $HONH_3ClO_4$ in a 16 ml sickle gauge developed four mm Hg pressure in 20 minutes at 73°C. This pressure remained constant for 285 minutes through temperatures of 81°C, 90°C, and 100°C. The following day the same sample developed four mm Hg at 110°C, 16 mm Hg at 120°C, and 20 mm Hg at 125°C the aggregate time of exposure was 385 minutes on the second day. Raised to 130°C on the third day, the sample developed 20 mm Hg immediately and decomposed irregularly thereafter as evidenced by a steady rise in pressure. Thus the sample could be conveniently dried at 70°C to 80°C and the approximate threshold of decomposition occurs at 130°C.

2. Kinetics of Decomposition

Thermal decomposition experiments have been performed on 98.5 percent pure nonaqueous material at 130°C and 140°C with only limited repeatability. Although mathematical description of the n/No versus t curve (where n = moles of gaseous products and No = moles of starting material) is still impossible, certain characteristics of the curves are found in all cases. The pressure rises in an acceleratory manner up to $n/No \cong 0.08$, then dP/dt decreases from n/No = 0.08 to n/No = 0.110. From 0.110, the rate of pressure evolution increases rapidly in a roughly parabolic fashion. Generally speaking, a higher No reduces repeatability, as evidenced by runs H-2 and H-3, see Figure 1. (0.200 gm each as opposed to ~0.100 gm used in others). The reproduction of the curve is not very adequate in any case, however, and may have much to do with possible contamination by traces of metal ions. The scattered curves obtained to date are contained in Figure 1.

3. Stoichiometry

Residues of the 0.200 gm runs froze immediately on removal from the high temperature bath into solid cakes slightly tinted brown or yellow. Infrared and ultraviolet spectroscopy failed to identify any species other than $HONH_3^+$ and ClO_4^-. Residues of the other runs were clear, colorless liquids freezing in the approximate region of 40°C.

Mass spectrographic analyses of the gaseous products indicated a very consistent ratio of 4/1, N_2O/HCl; no oxygen was detected. The decrease in pressure on removal from the high temperature bath corresponded to what would be expected from the ideal gas law, indicating that no unidentified vapors were produced. The ratio rose to 13/1 in run (H-7), which decomposed more rapidly than expected, indicating the possibility of some catalysis. With this exception, and infrequently detected trace quantities such as Cl_2, NO, N_2, the proportions of the vapor remained constant.

No tests were performed on the residues because the quantity was too small to remove from the gauge satisfactorily. In one run (H-5) the quantity of nitrous oxide detected accounted for 89 percent of the nitrogen available at the beginning of the run, indicating that the residue contains little if any material other than excess perchloric acid. The stoichiometry, as a very premature guess, should follow the form:

$$8H_3NOHClO_4 \longrightarrow 4N_2O + HCl + 7HClO_4 + 8H_2O + ?$$

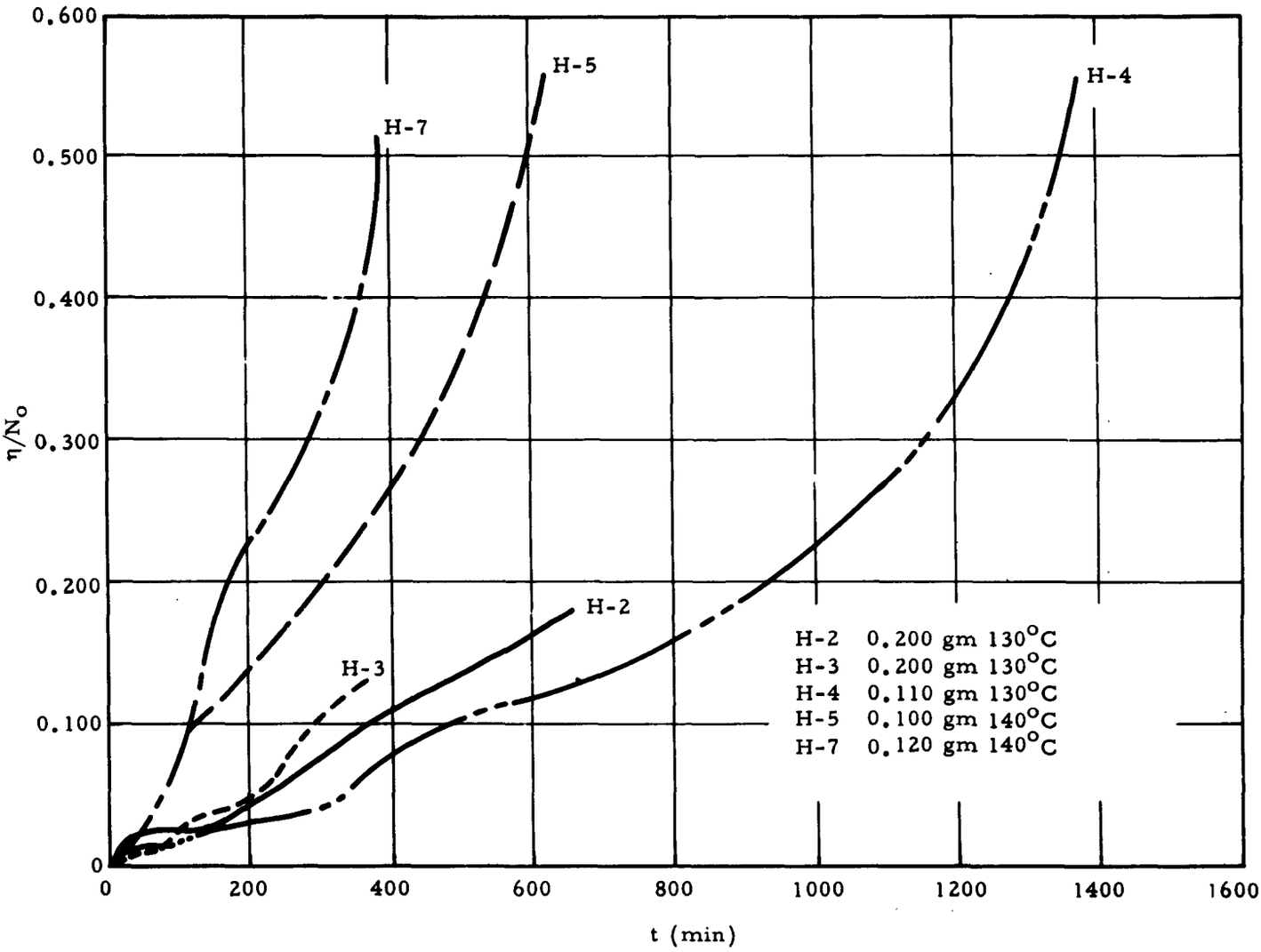

Figure 1. The Thermal Decomposition of 98.5 Percent Pure $HONH_3ClO_4$ at 130°C and 140°C

This expression is consistent with the observed phenomena, although it does not represent a conclusive and balanced equation.

D. DISCUSSION

Hofman and Kroll (Ref 6) while studying the thermal decomposition of hydroxylammonium hydrochloride at 150°C, discovered that the reaction is best described by two competing stoichiometric expressions:

(a) $3H_2NOH \longrightarrow N_2 + NH_3 + 3H_2O$

(b) $4H_2NOH \longrightarrow N_2O + 2NH_3 + 3H_2O$

The ordinary ratio of a/b = 5/7 can be increased by addition of basic substances or decreased by addition of acids; the proportions are independent of temperature and dilution. The proposed reaction path involves the dehydration of three moles of hydroxylamine to form the reactive species: $HON(NH_2)_2$, which, to follow equation (b), recombines with one mole of water to yield nitrous acid and two moles of ammonia. Nitrous acid then oxidizes a fourth mole of hydroxylamine, producing nitrous oxide and two moles of water. The $HON(NH_2)_2$ may also decompose directly to ammonia, nitrogen, and water, resulting in equation (a).

The obviously unsatisfactory intermediate $HON(NH_2)_2$ is replaced in a different explanation by Kurtenacker and Werner (Ref 7). The interaction of two hydroxylamines produces a hydroxy-hydrazine:

$$2H_2NOH \longrightarrow H_2NNHOH + H_2O$$

This intermediate tautomerizes and decomposes to ammonia and a new radical:

$$H_2NNHOH \longrightarrow H_3NNOH \longrightarrow NH_3 + \cdot NOH$$

The $\cdot NOH$ can then dimerize and lose water, producing nitrous oxide, or can combine with a third hydroxylamine to produce nitrogen and water.

$$2 \cdot NOH \longrightarrow HONNOH \longrightarrow H_2O + N_2O, \text{ or}$$

$$\cdot NOH + NH_2OH \longrightarrow N_2 + 2H_2O$$

This reaction scheme adequately explains the experimentally observed expressions and is the first mention of hyponitrous acid as the intermediate in the production of nitrous oxide (hyponitrous acid anhydride).

The existence of hyponitrous acid as the intermediate in decomposition of hydroxylammonium nitrite was conclusively demonstrated by Audrieth (Ref 8) who precipitated the silver salt by addition of $AgNO_3$. Thus the decomposition of hyponitrous acid to nitrous oxide and water was proven, although under somewhat different conditions of formation.

The decomposition of solid hydroxylamine at -25°C was found by Bodenstein (Ref 9) to follow the equation:

$$4H_2NOH \longrightarrow N_2O + 2NH_3 + 3H_2O$$

In the same study the oxidation of hydroxylamine to ·NOH and H_2O was confirmed, while the reaction of ammonia and hydroxylamine to produce nitrogen, water, and hydrogen was disproven.

The oxidation of hydroxylamine by hypochlorite and hypobromite was found by Riley, et al (Ref 10) to favor the production of nitrous oxide above nitrogen. The same species (hypohalides) oxidized hydrazine preferentially to nitrogen rather than nitrous oxide.

The decomposition of hydroxylammonium perchlorate is visualized as proceeding by a process analogous to that previously proposed for hydrazinium perchlorate. The initiating steps are the dissociation of the salt by proton transfer and decomposition of the perchloric acid to yield hydroxyl and chloryl radicals:

$$HONH_3^+ ClO_4^- \longrightarrow HONH_2 + HOClO_3 \qquad (1)$$

$$HOClO_3 \longrightarrow HO\cdot + ClO_3 \qquad (2)$$

The hydroxyl radical acts as a monodelectronator:

$$HO\cdot + HONH_2 \longrightarrow H_2O + HO\cdot NH \qquad (3)$$

The HON·H radical may then dimerize, after which the chloryl radical acts as a didelectronator (4), or the chloryl radical may react as a monodelectronator on the HNO$\dot{N}$H radical producing :$\dot{N}$OH, which then dimerizes (5).

$$2\dot{H}O\dot{N}H \longrightarrow HO\overset{H}{\dot{N}}-\overset{H}{\dot{N}}OH \xrightarrow{ClO_3} HONNOH + ClO_2 + H_2O \qquad (4)$$

$$\dot{H}O\dot{N}H + \dot{C}lO_3 \longrightarrow HOClO_2 + \dot{N}OH;\ 2\dot{N}OH \longrightarrow HONNOH \qquad (5)$$

It would seem logical that step (5) would be preferred to follow step (3); step (3) should be very rapid with respect to step (2), so the reactive species should be in close proximity. The decomposition of the hyponitrous acid thus formed to nitrous oxide and water should follow rapidly.

The autocatalytic nature of the reaction may be explained by competition between the water formed and the hydroxylammonium ion:

$$H_2O + H_3\overset{+}{N}OH \rightleftharpoons H_3O^+ + H_2NOH$$

a displacement reaction analogous to that proposed in the decomposition of hydrazine perchlorate, where ammonia displaces hydrazine:

$$NH_3 + N_2H_5^+ \longrightarrow NH_4^+ + N_2H_4$$

(Although water is a much weaker base than ammonia, H_2NOH is a much weaker base than N_2H_4 as can be seen from their respective dissociation constants The water would appear in the residue as OH_3ClO_4.

The curiosity of the "bump" in the curve at n/No = 0.100 remains to be explained. It cannot represent the decline in rate of decomposition of H_2NOH and beginning of autocatalytic decomposition of hydronium perchlorate, since the vapor samples taken at the slowest portion of the curve are uniform with those obtained at n/No$\sim$0.500-0.800. An approximate explanation suggests itself in the fact that ammonia is produced in the decomposition of H_3NOHCl mentioned above, and would be expected to appear here. It is probable that ammonia <u>is</u> formed, and reacts with hydroxylammonium ion to produce ammonium ion and hydroxylamine. This should at first catalyze the reaction by increasing the hydroxylamine concentration, then cause a slow down, since the NH_4^+ ion is much more stable than the H_3NOH^+ ion and the possibility of the initiating proton transfer to form perchloric acid is radically reduced. There is, however, more hydroxylamine consumed than ammonia produced, so there should be a considerable amount of hydronium perchlorate available to act as oxidizer. This ammonium perchlorate that may be formed would be oxidized back to hydroxylamine, then to nitrous oxide. The reaction would become more and more rapid as the relative concentration of the hydronium perchlorate increased.

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9. M. Bodenstein, Z. Elektrochem., 47, 501 (1941).

10. R. F. Riley, et al, J. Am. Chem. Soc., 76, 3301 (1954).

Thiokol
REACTION MOTORS DIVISION

SECTION VI

Task 56

CHEMISTRY OF DIFLUORODIAZINE AND OF NITROSYL FLUORIDE

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Report RMD 5043-64-F

RMD Project 5043, Task 56
Report Period: 1 January 1964 to
31 December 1964

Contract No. NOnr4364(00)
ARPA Order No. 417
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FOREWORD

This section of the report summarizes the results of a study of the chemistry of difluorodiazine and of nitrosyl fluoride during the period from 1 April 1964 to 31 December 1964 under Contract NOnr 4364(00), ARPA Order No. 417.

Personnel directly involved on this study were: A. R. Young, II (Project Supervisor), D. Moy (Principal Investigator), J. Dvorak, and J. Crothamel. Analytical support was contributed by R. Storey, B. Fagan, R. Crooker, D. Kates, and A. Fremmer.

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I. INTRODUCTION

Research efforts on this program during the reporting period were directed toward the following goals:

a. Characterization and chemistry of a new N-F species, the fluorodiazonium ion, $N_2F^{\oplus}$

b. Study of chemistry of cis-N_2F_2, trans-N_2F_2, and NOF·3HF

c. Synthesis of cis- and trans-difluorodiazine

d. Characterization of an adduct formed between tetrafluorohydrazine and arsenic pentafluoride.

Fluorodiazonium hexafluoroarsenate is conveniently prepared from cis-difluorodiazine and arsenic pentafluoride (Ref 1). The synthesis and characterization of the adduct as an ionic diazonium salt are described in detail in Section II of this report. Numerous reactions of this adduct were studied in the attempt to synthesize either new, highly-energetic fluorodiazonium salts or covalent oxidizing compounds containing the fluorodiazo group. Of these, methathesis reactions of fluorodiazonium hexafluoroarsenate in anhydrous hydrogen fluoride with salts of highly-energetic anions appear to be the most promising to date. Attempts to synthesize other fluorodiazonium salts directly from cis-difluorodiazine under normal conditions of temperature and pressure have been unsuccessful.

During the period covered by this report, the laboratory supply of difluorodiazine was exhausted. Since this compound is no longer available commercially, considerable time and effort were expended while attempting to synthesize this reagent in gram quantities. During this phase of work, a solid product was obtained from the reaction of tetrafluorohydrazine and arsenic pentafluoride. The stoichiometry of the product has not been determined precisely, although studies to date suggest an N_2F_4:AsF_5 mole ratio between 1:1 and 1.5:1.

II. MANUSCRIPT OF PAPER FOR PUBLICATION

The Preparation of Fluorodiazonium Herofluoroarsenate ($N_2F^+AsF_6^-$) From cis-Difluorodiazine

Prepared for Submission to
Journal of the American Chemical Society

[Contribution from the Chemistry Department, Reaction Motors Division, Thiokol Chemical Corporation, Denville, N.J.]

The Preparation of Fluorodiazonium Herofluoroarsenate ($N_2F^+AsF_6^-$) From cis-Difluorodiazine [1]

1. Presented at the 148th National Meeting of the American Chemical Society, Chicago, Illinois, September 1964.

David Moy and Archie R. Young, II

cis-Difluorodiazine and arsenic pentafluoride react at or below room temperature to yield a 1:1 solid adduct. The solid is stable under a dry atmosphere to 150°C. It reacts violently with water evolving nitrous oxide, but forms stable solutions in anhydrous hydrogen fluoride. Evidence obtained from infrared and F^{19} nuclear magnetic resonance spectra support an ionic structure for the product, $N_2F^+AsF_6^-$. The fluorodiazonium ion is believed to have a linear configuration, $:N{\equiv}\overset{+}{N}F$, as found in the isoelectronic nitronium ion. Fluorodiazonium hexafluoroarsenate is the first example of a stable derivative of a cation containing only nitrogen and fluorine.

INTRODUCTION

Difluorodiazine was first prepared by Haller[2] in 1942. Its electron diffraction pattern is consistent with a mixture of cis and trans isomers.[3]

2. J. Haller, Doctoral Dissertation, Cornell University, Ithaca, N.Y., September 1942.

3. S. Bauer, J. Am. Chem. Soc., 69, 3104(1947).

Colburn, et al.[4] first separated the isomers and showed that the infrared

4. C. Colburn, et al , J. Am. Chem. Soc., 81, 6397(1959).

spectrum of the higher melting isomer was consistent with a trans configuration. The results of a recent nuclear magnetic resonance study[5] appear to confirm the assignment of a cis configuration to the lower melting isomer.

5. J. Noggle, et. al., J. Chem. Phys., 38, 169(1963).

We are investigating the chemistry of difluorodiazine with particular emphasis on determining whether it can undergo addition reactions at the N=N double bond. Upon examining the possibility of using arsenic pentafluoride as an acid catalyst for such addition reactions, it was observed that cis-difluorodiazine reacted with arsenic pentafluoride to yield a stable white solid. An investigation of the preparation, composition, and structure of this solid was undertaken. The results indicate that the solid is an inorganic diazonium salt, $N_2F^+AsF_6^-$.

EXPERIMENTAL

Materials

Arsenic pentafluoride was obtained from Peninsular Chem Research and contained silicon tetrafluoride and boron trifluoride impurities in small amounts (< five percent). cis-Difluorodiazine was obtained from Air Products, Inc. and contained trans-difluorodiazine (approx eight percent) as the principal impurity. Nitronium hexafluoroarsenate was obtained from Ozark-Mahoning, Inc. The materials were used without further purification.

Preparation of cis-$N_2F_2 \cdot AsF_5$

Quantities of cis-difluorodiazine and arsenic pentafluoride were measured separately in a one-liter Monel bulb and then condensed into a Kel-F reaction tube at -196°C. The tube was allowed to warm to room temperature, and after one to two hours, the residual pressure in the tube was measured and gas samples were taken for infrared analysis. The white solid product was pumped for several hours to remove traces of volatile impurities (SiF_4, BF_3, and trans-N_2F_2). The product was removed from the reaction tube in a dry nitrogen atmosphere box and stored under nitrogen in Kel-F vials.

Under the same conditions, trans-difluorodiazine did not react with arsenic pentafluoride.

Analysis of cis-$N_2F_2 \cdot AsF_5$

1. Elemental Analysis

Independent N, F, and As analyses were performed on the solid adduct with the following results:

Anal. Calcd. for $N_2F_2 \cdot AsF_5$:	N, 11.88; F, 56.36; As, 31.76
Found :	N, 11.83; F, 56.79; As, 31.59.

2. Mass Spectrum

A Monel tube containing a small sample of the adduct was attached to a Bendix-Time-Of-Flight mass spectrometer (Model 12-101), evacuated and heated to 150°C. The cracking pattern obtained is presented in Table II.

3. Hydrolytic Decomposition

Two samples, 0.172 gm and 0.269 gm, of the solid adduct produced 0.67 mmole nitrous oxide (theory for $N_2F_2 \cdot AsF_5$, 0.73 mmole) and 1.12 mole nitrous oxide (theory for $N_2F_2 \cdot AsF_5$, 1.14 mole), respectively, on reaction with water in a closed Kel-F tube. N_2O was distilled from the reaction tube at -80°C and identified by its infrared spectrum.

4. Reaction with Sodium Fluoride in Hydrogen Fluoride

Anhydrous HF was obtained by reacting water-contaminated HF with the solid adduct until N_2O was no longer evolved. The anhydrous HF was then distilled onto a fresh sample of the adduct. The adduct dissolved readily above 0°C, and could be recovered unchanged upon removal of the HF.

Excess NaF was added to a solution of 0.205 gm of the solid adduct in HF. The reactor was cooled to -80°C, and 0.85 mmole of gas was distilled out of the reactor. On the basis of its infrared spectrum, the gas was estimated to be 95+ percent or 0.81 mmole cis-N_2F_2 (theory for $N_2F_2 \cdot AsF_5$, 0.87 mmole), the balance being N_2O.

Characterization of cis-$N_2F_2 \cdot AsF_5$

1. Infrared Spectrum

A conventional low temperature infrared cell constructed of Pyrex with an internal silver chloride plate supported on a hollow copper block was used to obtain a spectrum of cis-$N_2F_2 \cdot AsF_5$. Arsenic pentafluoride and cis-difluorodiazine were condensed onto the silver chloride plate at -196°C. The cell was pumped as the plate warmed to room temperature. A thin film of solid remaining on the plate at room temperature was scanned on a Perkin-Elmer Model 21 spectrometer from two to 15μ.

2. F^{19} Nuclear Magnetic Resonance Spectrum

The F^{19} NMR spectrum of a solution of the adduct in anhydrous HF (approx 40 percent solution) was obtained on a Varian HR-60 spectrometer at room temperature. Trifluoroacetic acid (TFA) was used as an external reference. Approximate chemical shifts (uncorrected for bulk susceptibility effects) and N-F coupling constants were obtained from the location of TFA side bands with an accuracy of ± 10 cps. A Teflon tube (six inches by 0.5 inch) fitted to a valve and ball joint by means of Swagelok connections was used as a sample tube. A sealed Kel-F capillary containing TFA was inserted directly into the sample tube.

3. Powder Diffraction Pattern

Powder diffraction patterns were obtained on samples of the adduct from spearate preparative runs and on samples recovered from HF solutions. All the patterns were identical. The patterns were photographed with CuKα radiation from a nickel filter. The x-ray samples were sealed under nitrogen in Pyrex capillaries.

4. Density

The density of a perfluorinated ether, FC-75[6], with which the adduct was compatible, was determined to be 1.77 gm/ml at 25°C. The density of

6. Trade name, Minnesota Mining and Manufacturing Company.

the solid adduct at 25°C was determined to be 2.6 gm/ml by displacement of FC-75.

DISCUSSION OF RESULTS

Stoichiometry of Solid Adduct

The data presented in Table I show that arsenic pentafluoride and cis-difluorodiazine react in a 1:1 mole ratio as indicated by equation 1.

$$\text{cis-}N_2F_2 + AsF_5 \longrightarrow N_2F_2 \cdot AsF_5 \qquad (1)$$

TABLE I

PREPARATION OF $N_2F_2 \cdot AsF_5$

Initial Reagents		Volatile Products Recovered (mmole)	
N_2F_2 (mmole)	AsF_5 (mmole)		
1.0	1.0	<0.2	trans-N_2F_2, SiF_4, BF_3
2.0	1.0	~1.0	cis-N_2F_2, trans-N_2F_2, SiF_4, BF_3
1.0	2.0	~1.0	AsF_5, trans-N_2F_2, SiF_4, BF_3

The only gases recovered when equimolar quantities of the reagents were mixed were SiF_4, BF_3 and trans-N_2F_2, all of which were present initially as impurities. The use of an excess of either reagent resulted in the quantitative recovery of that portion of reagent in excess of the equimolar amount. The results of separate fluorine, arsenic, and nitrogen analyses substantiate the 1:1 stoichiometry.

Arsenic pentafluoride does not react with trans-difluorodiazine under the conditions which lead to a stable adduct with the cis isomer. The difference in reactivities of the cis and trans isomers toward arsenic pentafluoride parallels their different reactivities toward glass and mercury.[7]

7. C. Colburn, et al, J. Am. Chem. Soc., 80, 5004(1958).

In addition to the elemental analyses and preparative data, the stoichiometry of the solid adduct can be inferred from the results obtained on reacting it with water and with sodium fluoride. The reaction with water consistently produced quantities of nitrous oxide in excellent agreement with the theoretical quantities predicted by equation 2. Difluorodiazine itself does not undergo

$$N_2F_2 \cdot AsF_5 + H_2O \longrightarrow N_2O + HF + HAsF_6 \qquad (2)$$

acidic or basic deomposition in water in the absence of reducing agents.[8]

8. M. Schmeisser and P. Sartori, Angew. Chem., 71 523(1959).

The reaction with sodium fluoride in hydrogen fluoride also serves to confirm the 1:1 stoichiometry. The total nitrogen recovered as cis-difluorodiazine and nitrous oxide was in excess of 98 percent of the theoretical quantities predicted by equation 3.

$$N_2F_2 \cdot AsF_5 + NaF \xrightarrow{HF} \text{cis-}N_2F_2 + NaAsF_6 \qquad (3)$$

The presence of a small amount of water in the sodium fluoride could account for the nitrous oxide formation via the rcaction shown in equation 2.

The mass spectrum at 150°C (Table II) shows only peaks that would arise from a mixture of cis- and trans- difluorodiazine and arsenic pentafluoride. Ion fragments with elements other than nitrogen, fluorine and arsenic were not found. The adduct has essentially no vapor pressure at 25°C, but can be transferred by vacuum sublimation at temperatures as low as 75°C. Some decomposition of the adduct occurs during sublimation due to the formation of trans-N_2F_2 which will not recombine with AsF_5 on cooling the gaseous mixture.

TABLE II

MASS SPECTRUM $N_2F_2 \cdot AsF_5$ AT 150°C

M/e	Ion	Relative Intensity
19	F^+	8.9
28	N_2^+	93.0
33	NF^+	5.2
47	N_2F^+	93.0
66	$N_2F_2^+$	3.1
75	As^+	6.0
94	AsF^+	6.2
113	AsF_2^+	8.6
132	AsF_3^+	14.2
151	AsF_4^+	100.0

Characterization of the Adduct as a Fluorodiazonium Salt

The chemical and mass spectral analyses offer no conclusive evidence regarding the structure of the $N_2F_2 \cdot AsF_5$ adduct. The two most likely structures are: (1) a molecular adduct formed through interaction of the unshared electron pair on a nitrogen atom with an empty orbital on arsenic, and (2) an ionic salt formed by fluoride ion donation to arsenic pentafluoride. An intermediate structure, namely, one involving a single fluorine bridge from nitrogen to arsenic is considered highly unlikely since fluorine bridging does not occur in arsenic pentafluoride itself, as evidenced by its low boiling point (ca. -60°C). The fact that the reaction of the adduct with sodium fluoride in HF liberates only cis-difluorodiazine suggests that the solid is a molecular adduct, i.e., cis-difluorodiazine is displaced by the stronger base, fluoride ion. If a simple metathesis reaction occurred involving $N_2F^{\oplus}$ and $F^{\ominus}$ ions, one would expect to obtain both geometric isomers. On the other hand, neither cis-or trans-difluorodiazine undergo acidic or basic hydrolysis, in contrast to the rapid conversion of the adduct to nitrous oxide on contact with water. This result suggests that molecular difluorodiazine is not present in the adduct. The infrared and F^{19} NMR spectra of the adduct offer convincing evidence that it is ionic. X-ray powder diffraction data also support this conclusion.

The infrared spectrum of a thin film of the solid adduct (Figure 1) shows only one absorption in the region normally assigned to N-F stretching vibrations. We attribute this band at 1050 cm^{-1} to the N_2F^+ cation. If the adduct were a molecular complex one would expect to observe two N-F stretching bands as in the case of cis-difluorodiazine[9], which absorbs at 896 cm^{-1} and at 952 cm^{-1}.

9. R. Sanborn, J. Chem. Phys., 33, 1855(1960).

The appearance of the N-F stretching absorption at a higher frequency in the adduct is indicative of the bond shortening one would expect in an ion such as $N{\equiv}\overset{+}{N}F$. The broad absorption, centered at 715 cm^{-1} is in the region normally assigned to the hexafluoroarsenate anion.[10] The F^{19} NMR spectrum of a 40

10. R. Peacock and D. W. A. Sharp, J. Chem. Soc., 2762(1959).

percent solution of the adduct in anhydrous hydrogen fluoride shows a fluorine on nitrogen triplet at a chemical shift of -179.4 ppm from trifluoroacetic acid (Figure 2). The observed N-F coupling constant (J_{N-F}) is 328 cps, or greater than twice the N-F coupling constants observed for cis- and trans-difluorodiazine[5] (Table III). The magnitude of the change in the N-F coupling constant on formation of the adduct is indicative of increased "s" character in the nitrogen bonding

TABLE III

F^{19} CHEMICAL SHIFTS AND N-F COUPLING CONSTANTS OF N-F COMPOUNDS

Compound	δ (ppm from CF_3COOH)	J_{N-F} (cps)
NF_3[5]	-200	155
cis-N_2F_2[5]	-228	145
trans-N_2F_2[5]	-167	136
N_2FAsF_6	-179.4	328

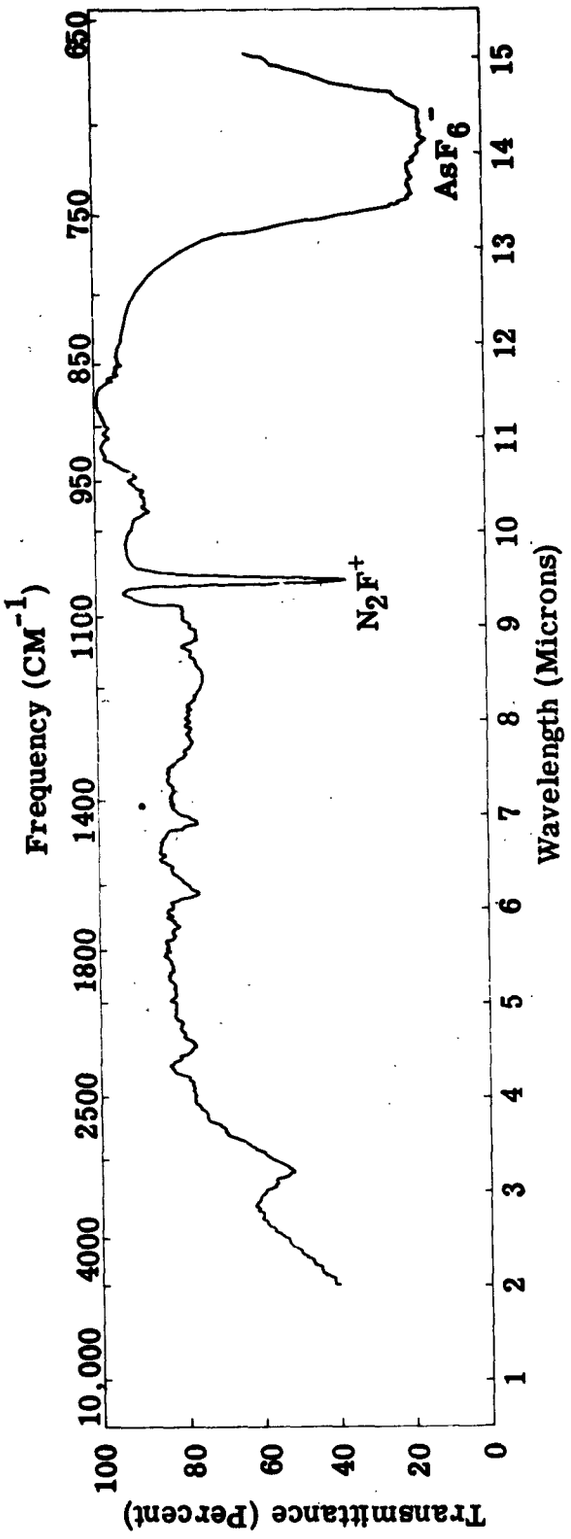

Figure 1. Infrared Spectrum of $N_2F^+AsF_6^-$ Film on AgCl

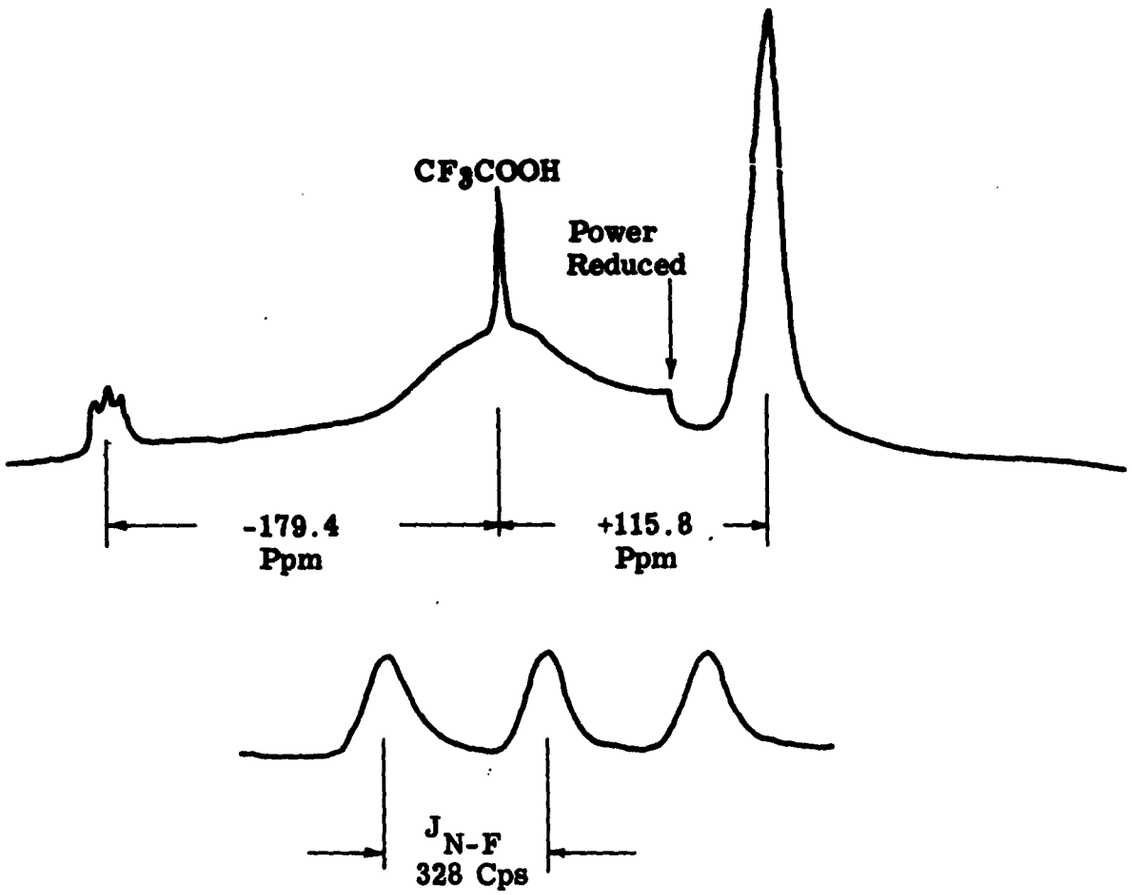

Figure 2. F^{19} NMR Spectrum of N_2FAsF_6 in Anhydrous HF

ortibals[11]. Such a change in bond hybridization would occur in going from

11. E. Muetterties and W. Phillips, "The Use of NMR in Inorganic Chemistry," Advances in Inorganic Chemistry and Radiochemistry, V. 4, p. 244, Academic Press, New York (1962).

FN=NF (sp^2) to $N\equiv\overset{+}{N}F$ (sp), but would not occur upon formation of a molecular complex from difluorodiazine and arsenic pentafluoride. Moreover, any reasonable structure for a 1:1 molecular addition compound would involve non-equivalent N-F fluorine atoms and hence should produce a more complex NMR spectrum than actually observed. There is no F^{19} resonance peak assignable to the hexafluoroarsenate ion in the spectrum obtained at room temperature (Figure 2), and the HF peak is displaced by approximately 10 ppm upfield relative to pure hydrogen fluoride. These observations indicate rapid fluoride exchange between HF and AsF_6^- at room temperature. The same results were obtained for a solution of sodium hexafluoroarsenate in hydrogen fluoride at room temperature. Neither fluorodiazonium hexafluoroarsenate nor sodium hexafluoroarsenate is sufficiently soluble in hydrogen fluoride at lower temperatures to permit observation of an NMR spectrum under conditions of slow fluoride exchange.

Finally, the x-ray diffraction pattern of N_2FAsF_6 is almost identical to that of NO_2AsF_6 (Table IV). One would expect the two salts to be isomorphous on the basis that NO_2^+ and N_2F^+ ions are both linear and being isoelectronic, should be nearly the same size.

Properties of Fluorodiazonium Hexafluoroarsenate

The fluorodiazonium salt is a white solid that decomposes without melting at 150°C. Its density at 25°C is 2.6 gm/cc. The salt may be sublimed *in vacuo* at 75°C and is stable in glass, Kel-F, or metal systems. It is very soluble and stable in anhydrous hydrogen fluoride at room temperature, but is rapidly decomposed by water, arsenic trifluoride, chlorine trifluoride, bromine trifluoride, trifluoroacetonitrile, and perfluoroacetic anhydride.

Conclusions

A 1:1 solid adduct is obtained by the reaction of *cis*-difluorodiazine with arsenic pentafluoride. The infrared and F^{19} nuclear magnetic resonance spectra of this adduct strongly indicate an ionic constitution. On the basis of the

magnitude of the observed N-F coupling constant it is concluded that the fluorodiazonium ion is linear ($F-\overset{+}{N}\equiv N$). The similarity of the x-ray pattern of fluorodiazonium hexafluoroarsenate to that of nitronium hexafluoroarsenate supports this conclusion. The reaction of the fluorodiazonium ion with sodium fluoride in hydrogen fluoride produces only cis-difluorodiazine rather than a mixture of geometric isomers. A simple explanation of this observation is not immediately apparent.

ACKNOWLEDGMENTS

We wish to acknowledge the contributions of Dr. D. Kates and Messrs. R. N. Storey, B. Fagan, and R. Crooker in performing instrumental analysis, and Mr. J. Crothamel, who carried out some of the preparative runs. This research was supported by the Advanced Research Projects Agency and monitored by the Office of Naval Research under Contract NOnr 4079(00).

TABLE IV

POWDER DIFFRACTION PATTERNS OF N_2FAsF_6 AND NO_2AsF_6

N_2FAsF_6		NO_2AsF_6	
I/I_o	d, Å	d, Å	I/I_o
20	5.18	5.17	5
80	4.92	5.03	20
		4.85	15
50	4.59	4.59	30
		4.46	30
		4.03	3
100	3.57	3.53	100
20	3.42	3.36	10
30	2.92	2.92	5
10	2.71	2.67	3
5	2.58	2.54	1
20	2.46	2.45	3
20	2.40	2.37	12
30	2.22	2.21	20
10	2.09	2.06	1
10	1.93	1.92	2
15	1.86	1.85	10
30	1.79	1.78	7
10	1.70	1.69	15
5	1.65	1.64	3
5	1.62	1.61	5
5	1.57	1.56	2
5	1.53		
5	1.47		
5	1.45	1.46	5
5	1.41	1.43	5
5	1.38		
5	1.31		
5	1.29		
5	1.28		

III. APPENDIX — THE CHEMISTRY OF THE FLUORODIAZONIUM ION

A. DISCUSSION

Several reactions of N_2FAsF_6 were examined in an attempt to isolate new oxidizing compounds containing the N_2F group either in covalent or ionic structures. The $N_2F^{\oplus}$ ion was found to be a strong oxidizer and to initiate free radical reactions upon being reduced. N_2FAsF_6 was found to undergo methathesis reactions in HF with oxygen-containing anions. However, these reactions yielded products which were unstable at room temperature in HF. With interhalogen anions, stable solutions were obtained in HF, and x-ray analysis of the resulting solids indicated that the intended methathesis reaction occurred to give stable products.

1. Oxidation-Reduction Reactions

a. Reaction with Nitric Oxide

N_2FAsF_6 quantitatively oxidized NO to $NOAsF_6$, according to equation 1.

$$NO + N_2FAsF_6 \xrightarrow{<25^{\circ}C} NOAsF_6 + \underline{cis}\text{-}N_2F_2 + N_2 \qquad (1)$$

The initial reaction probably involved the formation of a fluorodiazo radical (equation 2). The <u>cis</u>-difluorodiazine could arise in two ways as shown in

$$NO + N_2F^{\oplus} \longrightarrow NO^{\oplus} + N_2F\cdot \qquad (2)$$

equations 3 through 5.

$$2N_2F\cdot \longrightarrow N_2 + \underline{cis}\text{-}N_2F_2 \qquad (3)$$

$$N_2F\cdot + NO \longrightarrow NOF + N_2 \qquad (4)$$

$$NOF + N_2FAsF_6 \longrightarrow NOAsF_6 + \underline{cis}\text{-}N_2F_2 \qquad (5)$$

b. Reaction with Trifluoronitrosomethane

CF_3NO reacted rapidly with N_2FAsF_6 at -80°C to give $NOAsF_6$, fluorocarbons, $(CF_3)_2NONO$, CF_3NO_2, and $(CF_3)_2N\text{-}NO$. The initial reaction was probably as represented in equation 6. The $CF_3\cdot$ and $N_2F\cdot$ free radicals then initiated the dimerization of CF_3NO. It is probable that CF_3NO_2 and $(CF_3)_2N\text{-}NO$

$$CF_3NO \rightleftharpoons CF_3\cdot + NO\cdot \qquad (6a)$$

$$NO\cdot + N_2F^+ \longrightarrow NO^+ + N_2F\cdot \qquad (6b)$$

arose through decomposition of the dimer, $(CF_3)_2NONO$, followed by subsequent recombination of radicals.

c. Reaction with Trifluoromethyl Iodide

Further evidence of the very rapid free radical reactions initiated by the reduction of the $N_2F^{\oplus}$ ion was seen in the reaction of N_2FAsF_6 and CF_3I at low temperature (equation 7).

$$CF_3I + N_2FAsF_6 \xrightarrow{\geq -80^\circ C} IAsF_6\ (?) + \text{fluorocarbons},\ N_2,\ I_2 \qquad (7)$$

The initial reaction was probably the oxidation of CF_3I to $I^{\oplus}$ and $CF_3\cdot$ with the resultant reduction of $N_2F^{\oplus}$ to $N_2F\cdot$. It is of interest to note that CF_3I, CF_3NO, and NO do not react with <u>cis</u>- or <u>trans</u>-N_2F_2 below 100°C.

d. Reactions with Nitrosyl Chloride and Hydrogen Chloride

With gaseous NOCl or HCl, rapid oxidation of the chloride ion by the fluorodiazonium ion resulted in the liberation of Cl_2, N_2, and small amounts of <u>cis</u>-N_2F_2. No evidence for the coupling of the fluorodiazo radical either with itself, with NO, $CF_3\cdot$, or Cl radicals was observed in these reactions. Similarly, when the fluorodiazo radical was generated in the presence of the difluoramine radical, or in the presence of <u>trans</u>-difluorodiazine or perfluoroolefins, no coupling reactions were observed.

2. Metathesis Reactions

a. Reaction with Silver Perchlorate

$AgClO_4$ dissolved in HF reacted rapidly at room temperature with an HF solution of N_2FAsF_6, as shown in equation 8. The formation of N_2O and

$$AgClO_4 + N_2FAsF_6 \xrightarrow[25^\circ C]{HF} N_2O + ClO_3F + AgAsF_6 \qquad (8)$$

ClO_3F probably resulted from the decomposition of the unstable N_2FClO_4 as shown in equation 9.

$$[FN{=}N\text{-}O\text{-}ClO_3] \longrightarrow N_2O + ClO_3F \qquad (9)$$

b. Reaction with Ammonium Fluorosulfonate

NH_4SO_3F and N_2FAsF_6 reacted in HF at room temperature as shown in equation 10. As in the reaction with perchlorate, SO_2F_2 and N_2O probably arose

$$NH_4SO_3F + N_2FAsF_6 \longrightarrow NH_4AsF_6 + NO_2 + SO_2F_2 \qquad (10)$$

through decomposition of FN_2SO_3F.

c. Reaction with Dinitrogen Tetroxide

Liquid N_2O_4 reacted with solid N_2FAsF_6 at $-9^\circ C$ to give results similar to those obtained in the $AgClO_4$ and NH_4SO_3F reactions. The products were N_2O, cis-N_2F_2, NO_2F (trace), $NOAsF_6$, and NO_2AsF_6, and can be accounted for by the following reaction scheme (equations 11 and 12):

$$NONO_3 + N_2FAsF_6 \longrightarrow NOAsF_6 + [N_2F^{\oplus}\ NO_3^{\ominus}] \longrightarrow N_2O + NO_2F \qquad (11)$$

$$NO_2F + N_2FAsF_6 \longrightarrow NO_2AsF_6 + \text{cis-}N_2F_2 \qquad (12)$$

The failure to isolate fluorodiazonium perchlorate, fluorosulfonate, or nitrate in these experiments does not necessarily preclude the possibility that these compounds are isolable by metathesis in solution. Several variables must be investigated before making a final judgment on this possibility. These variables include:

- The effect of concentration on the rate of decomposition (rate of N_2O formation)
- The effect of temperature on the rate of decomposition
- The nature of the solvent.

In addition, the possibility must be examined that, although N_2F^+ and ClO_4^-, NO_3^-, or SO_3F^- ions react vigorously in the dissolved state, they may be stabilized in an ionic lattice.

d. Reaction with Tetrafluorochlorate or Tetrafluorobromate Ions

Metathesis reactions with cesium tetrafluorochlorate (or tetrafluorobromate) with N_2FAsF_6 in HF gave more promising results. These anions were highly fluorinated and in a high oxidation state, thereby greatly reducing the tendency of the $N_2F^{\oplus}$ to decompose by acting as a fluorinating or oxidizing agent. Mixtures of $CsClF_4$ (or $CsBrF_4$) and N_2FAsF_6 in HF gave stable solutions, and on removal of HF left an insoluble, gummy residue. X-ray diffraction patterns of the product from the $CsClF_4$-N_2FAsF_6 reaction snowed weak lines associated with $CsAsF_6$, as well as lines not assignable to $CsAsF_6$, $CsClF_4$, or N_2FAsF_6. Thus, the desired reactions (equations 13 and 14) may

$$N_2FAsF_6 + CsClF_4 \longrightarrow CsAsF_6 + N_2FClF_4 \qquad (13)$$

$$N_2FAsF_6 + CsBrF_4 \longrightarrow CsAsF_6 + N_2FBrF_4 \qquad (14)$$

have proceeded to give stable products and further studies will be conducted in an attempt to isolate N_2FClF_4 and N_2FBrF_4.

B. CHEMISTRY OF CIS-N_2F_2, TRANS-N_2F_2 AND NOF

1. Reactions of cis-Difluorodiazine with Fluoride Acceptors

The ease of preparation of the fluorodiazonium hexafluoroarsenate under mild conditions of temperature and pressure led us to explore the possible syntheses of new fluordiazonium salts directly from cis-difluorodiazine and suitable fluoride acceptors. Several potential fluoride acceptors were allowed to react with cis-difluorodiazine under a variety of conditions, ranging from atmospheric pressure at room temperature to moderate pressures (100 lb/in.^{2}) at 150°C. The attempted reactions included cis-N_2F_2 with BiF_5, PF_5, BrF_3, ClF_3, SO_3, SF_4, and SnF_4. None of these systems, under the conditions of the reaction, produced the desired fluorodiazonium salt. The only reaction observed was the fluorination of the substrate by difluorodiazine, with the subsequent decomposition of the latter to nitrogen and fluorine. However, a recent report (Ref 2) indicates that N_2FBF_4 and N_2FPF_6 can be prepared under very-high pressure conditions and it may be wise to reexamine some of these systems, notably N_2F_2-ClF_3 and N_2F_2-BrF_3, at very high pressures.

2. Reaction of trans-N_2F_2 with SbF_5

A solid product obtained by the reaction of trans-N_2F_2 with excess SbF_5 is currently being investigated. If the solid product is analogous to $N_2F^{\oplus}AsF_6^{\ominus}$, it might serve as a convenient source of cis-N_2F_2 according to the following scheme (equations 15 and 16):

$$\text{trans-}N_2F_2 + SbF_5 \longrightarrow N_2F^+SbF_6^- \qquad (15)$$

$$N_2F^{\oplus}\ SbF_6^{\ominus} + NaF \xrightarrow{HF} \text{cis-}N_2F_2 + NaSbF_6 \qquad (16)$$

Since only a small quantity of trans-N_2F_2 was available when this investigation was initiated, only a small amount of the solid was prepared. Consequently, the data obtained on the properties of this solid are of a preliminary nature.

An attempt was made to obtain an NMR spectrum of the solid in liquid HF. The only peak observed, however, was that of HF. In addition, an attempt was made to generate cis-N_2F_2 from the solid by treating it with NaF in HF. No evidence of the desired reaction was obtained.

Additional studies will be conducted when a sufficient amount of trans-N_2F_2 is available.

3. Attempted Reaction of NOF·3HF with cis-N_2F_2

A preliminary reaction between cis-N_2F_2 and NOF·3HF conducted in an NMR tube resulted in the isolation of a small amount of a white solid which had an x-ray powder pattern not previously encountered (Ref 1). When the reaction was repeated on a larger scale, to obtain a sufficient amount of solid for analysis, cis- and trans-N_2F_2 were recovered. However, a solid product was again isolated. The infrared spectrum of this solid showed an absorption at 2315 cm^{-1}, attributable to NO^+, and a broad band at 640 cm^{-1} with a shoulder at 720 cm^{-1}. When heated in the mass spectrometer, this solid was found to envolve large quantities of NO and HF, as well as trace quantities of NO_2, SiF_4, and C-F materials.

Since N_2F_2 was recovered from the reaction mixture and no N-F peaks were observed in the mass spectrum of the solid product, an investigation of the NOF·3HF used in the reaction was initiated. It was determined that pumping on the NOF·3HF at ambient temperatures yielded a solid residue which has an x-ray powder pattern consistent with that of the previously isolated solid. The infrared spectrum of this solid also shows an absorption at 2315 cm^{-1}, assigned to NO^+, and a band at 650 cm^{-1}. Again, large quantities of NO and HF were evolved when the solid was heated in the mass spectrometer. Present evidence indicates that this solid is a nitrosyl bifluoride-hydrogen fluoride complex, $NO^{\oplus}\ HF_2^{\ominus}\cdot 2HF$. Chemical analysis is presented in Table I.

TABLE I

ANALYSIS OF NOF·3HF SOLID

Atom or Group	%Found	%Calcd for $NOHF_2\cdot 2HF$
N	11.98	12.84
NO^+	29.04	27.52
F^-	56.47	69.72

The NMR spectrum of the distillate obtained from pumping on the NOF·3HF complex appeared to be consistent with pure HF. A hydrolysate of the distillate, however, gave a positive test for NO_2^-, indicating the presence of NO^+. Pumping on the distillate did not produce any additional solid, even after the distillate was allowed to stand at ambient temperatures for several weeks.

C. SYNTHESIS OF CIS- AND TRANS-DIFLUORODIAZINE

We have found that trans-difluorodiazine can be prepared safely and conviently in 50-60 mmole amounts by the decomposition (by treatment with NO) of a solid adduct formed between N_2F_4 and AsF_5. The gas-solid reaction proceeds well at room temperature or below without requiring careful temperature control. Up to 50 percent yields of trans-N_2F_2 (based on the amount of N_2F_4 reacted) have been obtained by this method. Since the reaction produces equivalent amounts of NF_3, the final purification of trans-N_2F_2 was accomplished by gas chromatography using a 10-foot molecular sieve 13X column.

In addition, a second method for the preparation of trans-difluorodiazine was attempted. Yields of trans-N_2F_2 up to 40 percent have been reported (Ref 3) by the reaction of N_2F_4 with $AlCl_3$. However, under static conditions and high N_2F_4 starting pressure (necessary for the synthesis of mode[illegible] [illegible]ie quantities of difluorodiazine), the yield of trans-difluorodiazine was [illegible] to be critically dependent on reaction conditions (such as contact time) that are difficult to control.

A recent report (Ref 4) describes a flow reaction system which may serve as a more convenient route to the trans isomer than either of the above methods.

Efforts to synthesize the cis isomer in large scale amounts have not been very rewarding. Glemser, et al (Ref 5) report high yields of both isomers by fluorination of sodium azide in a flow system followed by immediate decomposition of the resulting fluorine azide at 85°C to give difluorodiazine and nitrogen. An attempt was made to use this method in the RMD laboratory. However, deflagration occurred in the sodium azide reactor several minutes after the flow of diluted fluorine/nitrogen was initiated.

Both isomers of difluorodiazine arise as byproducts (one to 25 percent yield) in the synthesis of NF_3 by the electrolysis of molten ammonium bifluoride (Ref 6) at $\simeq$ 130°C. Unfortunately, it has been found that the yield of difluorodiazine at the beginning of the electrolysis is very low. The product collected after $\simeq$ 600 ampere-hours operation contained only one to two percent difluorodiazine, the remainder being nitrogen trifluoride. The yield of difluorodiazine

is expected to increase on prolonged operation of the cell. The electrolysis cell and its operation are described in the Experimental Section of this report.

D. TETRAFLUOROHYDRAZINE-ARSENIC PENTAFLUORIDE ADDUCT

1. Preparation

During the search for a convenient preparation for difluorodiazine from tetrafluorohydrazine, it was observed that a solid product is formed from the reaction of tetrafluorohydrazine and arsenic pentafluoride. The reaction proceeds slowly by allowing a mixture of N_2F_4 and AsF_5 to warm to room temperature in a glass or a Kel-F reactor. The yield and rate of formation of the solid product are dependent on the total pressure of reactants. The latter must be of the order of two to three atmospheres to attain 80 percent conversion of N_2F_4 to the adduct within 18 hours. It has not been determined whether the composition of the solid differs when varying the initial ratios of N_2F_4:AsF_5. Formation of the solid product is not a reversible process. Slow decomposition at room temperature results in the liberation of trans-N_2F_2 and NF_3; no N_2F_4 has ever been observed.

The solid product formed by the reaction is thermally unstable at room temperature as evidenced by the generation of trans-N_2F_2 and NF_3 during the 18-hour preparation. Upon removal of all residual gas pressure, after preparing and allowing the solid to remain at room temperature for four days, a slow evolution of trans-N_2F_2 and NF_3 (1:2 mole ratio respectively) occurred. A white solid residue was still present. However, no AsF_5 was observed in the gaseous phase.

2. Stoichiometry

Because of the thermal instability of the product, it has been very difficult to make a determination of its stoichiometry from preparative data. Approximate values have been obtained by measuring the amounts of original reactants and by analyzing, qualitatively and quantitatively, the gaseous fraction after the preparation of the solid product. These values have been inconsistent, usually giving calculated stoichiometry molar ratios of 1:1 to 3:2 (by mole ratio of N_2F_4:AsF_5 respectively) for the product. The inconsistent results probably arise from difficulties in the analytical procedure caused by the formation of trans-N_2F_2 and NF_3 during the preparation. Therefore, quantitative analysis involves separation of N_2F_4, NF_3, and trans-N_2F_2 by vapor-phase chromatography on a molecular sieve column and careful measurement of peak areas of

the resulting chromatograms. It is suspected that some loss of trans-N_2F_2 and NF_3 occurs on the 13X molecular sieve column.

Additional information on the stoichiometry of the solid was obtained by careful analysis of the products resulting from the reaction of the solid with NO. The gaseous fractions contained only unreacted NO, trans-N_2F_2, and NF_3; the latter two always occurring in a 1:1 mole ratio. According to infrared and x-ray analyses, only $NOAsF_6$ was present in the solid residue. These observations are consistent with an adduct of 3:2 (N_2F_4:AsF_5) stoichiometry as indicated by the reaction in equation 17.

$$NO + N_3F_6 \cdot AsF_5 \longrightarrow NOAsF_6 + NF_3 + \text{trans-}N_2F_2 \qquad (17)$$

A corresponding reaction with a compound of 1:1 stoichiometry ($N_2F_4 \cdot AsF_5$) would give a 3:2 mole ratio of trans-N_2F_2:NF_3 according to equation 18.

$$4NO + 4N_2F_4 \cdot AsF_5 \longrightarrow 4NOAsF_6 + 3\ \text{trans-}N_2F_2 + 2NF_3 \qquad (18)$$

3. Chemical Analysis

Elemental analyses for nitrogen (in the form of trans-N_2F_2 and NF_3) have been performed in an effort to determine the stoichiometry of this adduct. However, as with the preparative data, the results are not definitive. Decomposition of the solid with CsF in HF gave only trans-N_2F_2 and NF_3 and not N_2F_4 as expected and a total nitrogen content of 9.5 percent. Decomposition with NO (excess) gave 10.0 and 11.7 percent nitrogen, determined as NF_3 and trans-N_2F_4 on two runs (theoretical N for $N_2F_4 \cdot AsF_5$ is 10.3 percent; for $N_3F_6AsF_6$ is 12.9 percent). These analyses are subject to the same criticism expressed above (Part D.2).

4. Infrared and NMR Spectra

A mull of the solid product could not be prepared from the standard mulling agents because of its reactivity. An infrared scan of a sample of the solid pressed between two AgCl plates showed the typical broad absorption at 700 cm^{-1} indicative of the $AsF_6^{\ominus}$ ion and a broad, poorly-defined absorption centered at 910 cm^{-1}. It is not immediately apparent whether this band is associated with the difluoramino radical or ion, or with some other N-F species.

The solid adduct is very reactive toward anhydrous HF, SO_2, or IF_5, liberating trans-N_2F_2 and NF_3. On reacting with HF followed by removal of HF,

a white solid residue remained. A sample of this solid redissolved in HF gave no F^{19} NMR absorption other than that caused by HF and Freon 11 (used as reference). However, treatment of another sample of this residue with NO liberated trans-N_2F_2 and NF_3, showing the presence of an N-F species.

The reaction of the solid with liquid SO_2 resulted in a two-phase system. One phase was a gel; the second phase was a clear liquid. On removal of the SO_2, a white, solid residue remained. An F^{19} NMR spectrum of the two phase system showed a sharp singlet absorption at -75 ppm relative to Freon 11. The position and structure of this band was more indicative of S-F materials rather than N-F materials, which usually have resonances at frequencies further downfield than -75 ppm relative to Freon 11, and normally have fine structure because of N-F coupling.

5. X-Ray Diffraction Pattern

X-ray diffraction patterns of the solid product were obtained. The samples were prepared and run under the following conditions:

1. Immediately after preparation of the solid

2. After certain intervals during decomposition of the solid at room temperature

3. After reaction with HF and IF_5.

The major lines of the pattern of the freshly-prepared solid product (Table II) were not identifiable as any known pattern. However, the pattern contained weakly-to-moderately intense lines because of $NOAsF_6$, O_2AsF_6, or some isomorphous material (such as $NFAsF_6$). After standing at room temperature for two weeks, the diffraction pattern (Table III) was identical with that of $NOAsF_6$, except for three very weak lines. The 4.46 line (most intense in Table II) was still apparent. After treatment with HF or IF_5, the patterns (Table IV) were identifiable as $NOAsF_6$. The diffraction pattern of $NOAsF_6$ is included for comparison.

TABLE II

X-RAY DIFFRACTION PATTERN OF FRESHLY-PREPARED $N_2F_4 \cdot AsF_5$ PRODUCT

d, Å	I/I_o
5.37	50
4.93	3
4.67*	10
4.46	100
4.03*	10
3.77	1
3.39	50
3.24	1
2.84*	5
2.70	15
2.58	1
2.45	1
2.31*	10

*Lines present in $NOAsF_6$ or O_2AsF_6

TABLE III

X-RAY DIFFRACTION PATTERN OF $N_2F_4 \cdot AsF_5$ PRODUCT AFTER DECOMPOSITION AT ROOM TEMPERATURE

d, Å	I/I_o
5.16*	3
4.67	100
4.48*	2
4.04	100
3.17*	1
2.86	40
2.44	7
2.33	12
2.02	5
1.86	10
1.81	20
1.65	15
1.45	10

*Lines not present in $NOAsF_6$ or O_2AsF_6

TABLE IV

X-RAY DIFFRACTION PATTERN OF N_2F_4-AsF_5 PRODUCT AFTER TREATMENT WITH HF OR IF_5, AND OF $NOAsF_6$

N_2F_4-AsF_5 + HF		N_2F_4-AsF_5 + IF_5		$NOAsF_6$	
d, Å	I/I_o	d, Å	I/I_o	d, Å	I/I_o
4.91	10	---	---	---	---
4.65	100	4.67	S	4.67	100
4.02	100	4.05	S	4.05	100
3.82	10	---	---	---	---
3.68	2	3.68	W	---	---
3.26	2	---	---	---	---
3.14	10	---	---	---	---
2.85	35	2.84	S	2.84	40
2.44	5	2.44	M	2.44	10
2.32	8	2.34	M	2.34	20
2.13	3	---	---	---	---
2.02	10	2.03	W	2.03	8
1.85	5	1.86	M	1.86	15
1.80	10	1.81	M	1.81	25
1.65	10	1.65	M	1.65	20
1.59	1	---	---	---	---
1.55	5	1.56	W	1.56	15

E. EXPERIMENTAL

Experimental details of the work involving the synthesis and chemistry of N_2FAsF_6, the reactions of cis-N_2F_2, trans-N_2F_2, and NOF, and the preparation of trans-N_2F_2 are contained in previous reports (Ref 1).

1. Preparation of cis- and trans-Difluorodiazine

a. Fluorination of Sodium Azide

The procedure used to synthesize difluorodiazine is reported by Glemser, et al (Ref 5). The reactor consisted of a 24/40 standard taper -1-liter Monel eductor tube to allow sweepage of F_2/N_2 gas. The outlet of the eductor tube was connected to a six foot coil of 1/4 inch Monel tubing heated to 85°C. A series of glass U-traps cooled with liquid oxygen (-182°C) served to collect the products. The reactor was charged with a mixture of 150 gm of sodium azide (Matheson, Coleman, and Bell) and sodium fluoride pellets. The latter served not only as a diluent for the sodium azide, but also to reduce the free volume of the reactor and to diffuse the stream of F_2/N_2. The reactor mix deflagrated several minutes after the F_2/N_2 stream was started.

b. Electrolysis of Ammonium Bifluoride

A divided electrolysis cell made of nickel was used in this preparation. The dimensions of the cell were approximately six inches by six inches by 10 inches, with a capacity of eight pounds of molten ammonium bifluoride. The outer jacket of the cell served as the cathode. The anode compartment consisted of a 1/2-inch OD nickel tube extending down into the center of the cell and was insulated from the outer jacket by a Teflon sleeve and Teflon gaskets. This was enveloped by a two inch by two inch by six inch nickel rectangular tube dipping into the molten bath to serve as the divider. The divider was insulated from both the anode and cathode by Teflon gaskets. The temperature of the salt bath was determined by a thermometer insert dripping into the bath. Elevated temperatures were obtained by wrapping the entire cell with electrical heating tapes. Gas inlet and outlet tubes allowed for sweepage of the cathode compartment with helium. A Sel-Rex rectifier, Type SIC8KD, was used as the dc power supply.

The ammonium bifluoride was heated to 125°C (its melting point) and the cell was operated at 10 to 12 volts, 8 to 10 amps. Once the electrolysis was initiated, the heat of reaction was sufficient to maintain the cell temperature

between 135°C to 145°C and no external heat was necessary. The reaction product gases were swept from the cell by a stream of helium through a bed of sodium fluoride pellets, and then into a bank of traps cooled by liquid nitrogen. A six-hour run under these conditions normally gave 10 to 12 liquid cc's of product gases condensable at liquid nitrogen temperatures. The final separation of the products was accomplished by trap-to-trap distillation from -182°C to -196°C. Of the first 30 to 35 liquid cc's of product collected, only one to two percent was difluorodiazine. More than 90 percent of the product was NF_3; N_2O (and possibly NO) was present in small amounts. The gases were identified by infrared and mass spectral analyses.

2. Tetrafluorohydazine-Arsenic Pentafluoride Adduct

a. Preparation and Stoichiometry

Quantities (from 10 to 20 mmole each) of N_2F_4 and AsF_5 were condensed at -196°C into a high-pressure, Fisher-Porter glass reactor. The reactants were warmed slowly to room temperature and maintained at ambient temperature overnight. The formation of a white solid was observed immediately on warming. The total pressure of the system rose to ca. 80 to 100 psi, dropping to approximately 30 to 40 psi after 18 hours. No further decrease in pressure was observed on prolonged standing at room temperature. The gases were fractionated at -143°C and -196°C traps. Only AsF_5 was recovered in the -143°C traps, while the -196°C traps contained a mixture of N_2F_4, trans-N_2F_2, and NF_3. Chromatographic analysis on a 10-foot molecular sieve 13X column determined the relative amounts of each component, from which the total amount of each component could be calculated. From the final and initial gas compositions, the stoichiometry of the solid product ranged from 1:1 to 3:2 (N_2F_4:AsF_5 respectively). The results of two preparations are shown in Table V.

The solid reaction product was maintained at ambient temperature in the glass reactor for four days, during which time a slow build-up of gas pressure (condensable at -196°C) occurred. The gases were analyzed at the conclusion of four days and found to consist of a mixture of trans-N_2F_2 and NF_3 in a 1:2 mole ratio respectively. $NOAsF_5$ was observed.

b. Analysis

A solution of CsF in HF was reacted with a 161.4 mg sample of the freshly-prepared solid product, evolving a total of 0.73 mmole gaseous products. Infrared analysis showed trans-N_2F_2, NF_3, and NO; the latter perhaps resulting from water in the HF. VPC analysis showed 0.40 mmole trans-N_2F_2, 0.18 mmole

NF_3, and 0.14 mmole NO, giving a total nitrogen content of 9.55 percent theoretical for $3N_2F_4 \cdot 2AsF_5$ is 12.9 percent).

TABLE V

STOICHIOMETRY OF REACTION BETWEEN N_2F_4 AND AsF_5

	Run No. 1	Run No. 2
Original reactants (mmole)		
N_2F_4	32	32
AsF_5	32	21.3
Final gas composition (mmole)		
N_2F_4	5.5	19.7
AsF_5	14.8	10.7
trans-N_2F_2	0.25	0.12
NF_3	0.50	0.26
Amount of Reaction (mmole)		
N_2F_4	26.5	12.3
AsF_5	17.2	10.6
Ratio of N_2F_4/AsF_5		
	1.54/1	1.16/1

Two samples, 208 mg and 325 mg, of the freshly-prepared product gave 1.0 and 1.8 mmole of gaseous products (other than NO) when reacted with an excess of NO. Infrared and VPC analysis revealed the presence of trans-N_2F_2 and NF_3 in equivalent amounts. The total nitrogen contents were 10.0 and 11.6 percent, respectively, for the two samples. An x-ray diffraction pattern of the solid residue showed only lines typical of $NOAsF_6$.

c. Infrared and NMR Spectra

A small sample (approximately 25 mg) of the solid product from N_2F_4 and AsF_5 was pressed between two AgCl plates and scanned in a Perkin-Elmer 221 spectrophotometer from two to 15μ. Broad absorptions were observed at 910 cm^{-1} and 700 cm^{-1}. Paraffin oil could not be used as a mulling agent because of rapid attack on the oil by the solid.

Attempts were made to obtain an NMR spectrum of a 25 percent solution of the solid in HF using a Teflon sample tube. Anhydrous HF and Freon 11 (used as an internal reference) were distilled into the solid. As the mixture warmed to room temperature, rapid evolution of gases occurred. A scan of the F^{19} resonance region showed only HF and Freon 11 resonances. The gases over the liquid solution were analyzed and found to be trans-N_2F_2 and NF_3. A solid residue remained upon removal of HF. A larger sample of the residue left behind after treatment with HF was redissolved in anhydrous HF, but no F^{19} resonance other than that for HF was observable in the NMR spectrometer.

Attempts were made to use liquid SO_2 as a solvent for the NMR spectrum. On warming a mixture of SO_2 and the freshly-prepared solid product to room temperature, vigorous gassing occurred. This was accompanied by the formation of a two phase system; one, a viscous gel; the second, a clear solution. A scan in the NMR spectrometer showed a sharp singlet absorption at -75 ppm relative to Freon 11. Infrared analysis of the gases over the condensed phases showed only small amounts of trans-N_2F_2 + NF_3 and traces of a material believed to contain S-F bonds. Removal of the SO_2 left behind a moist, sticky, white residue which could not be further dried for x-ray analysis.

d. X-Ray Analysis

X-ray diffraction patterns were obtained using glass capillary sample holders. The samples were loaded under an inert atmosphere.

F. REFERENCES

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